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Intrinsic Bioremediation of Hydrocarbons at Cold Temperatures

by

Christopher Alan Johns

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

Department of Civil & Environmental Engineering

Edmonton, Alberta

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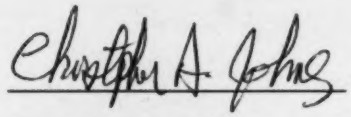

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ABSTRACT

This research project involved application of the intrinsic bioremediation methodology to cold temperature sites contaminated with petroleum hydrocarbons. A site investigation was carried out at two sites in Cold Lake, AB to delineate the stratigraphy, hydrogeology, microbiological setting, contaminant levels and geochemical conditions. Groundwater temperatures were approximately 8°C, which is colder than most sites where intrinsic bioremediation has been documented. At one site, dissolved benzene, toluene, ethylbenzene, and xylenes (BTEX) contamination was confined to a shallow sandy aquifer. At the second site, BTEX contamination was present between 2-4 metres depth within a slightly weathered glacial till deposit. An assessment of the terminal electron accepting processes was undertaken and enumeration of soil microorganisms was completed. A laboratory microcosm study investigated the effects of cold temperatures on the rate and extent of substrate utilization. Results indicate that intrinsic bioremediation is viable and ongoing at these cold temperature sites.

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LIST OF NOMENCLATURE AND ABBREVIATIONS

BTEX: Benzene, Toluene, Ethyl Benzene, and Xylenes

CCME: Canadian Council of Ministers of the Environment

ETL: Enviro-Test Laboratories, Edmonton

FFTA: Fire Fighter Training Area

LEL: Lower Explosive Limit

MPN: Most Probable Number

OIS: Old Imperial Site

PVC: Polyvinylchloride

QC: Quality Control

TEA: Terminal Electron Acceptor

TEAP: Terminal Electron Accepting Process

TEH: Total Extractable Hydrocarbons (C_{11}-C_{30})

TVH: Total Volatile Hydrocarbons (C_5 – C_{10})

TPH: Total Petroleum Hydrocarbons (C_5 – C_{30})

USEPA: United States Environmental Protection Agency

VOC: Volatile Organic Compound

Field Blank: A sample of distilled or deionized water taken from the laboratory out into the field, poured into a sampling vial at the site, closed, and returned as if it were a sample. The level of contamination of the field blank can be considered the zero analyte signal for determining the limit of detection.

Rinsate Blank: A sample of the final rinse of sampling mechanism before it is reused (put in a new well or inserted into the ground). It is used to evaluate whether a sample may have been contaminated from material taken in the previous sample.

Replicate Sample: A subsample of another sample which is labeled separately to estimate the precision of laboratory results.

Laboratory Blank: Similar to a Field Blank except that the distilled deionized water used in the laboratory at the time each batch of samples is received is analyzed in the same manner as other samples. This may detect contamination that occurs in the laboratory.

Standard Reference Sample: These samples have been analyzed previously by outside laboratories and can detect either instrument calibration error or the use of inappropriate laboratory analytical methods.

1 INTRODUCTION

Intrinsic bioremediation is the process whereby soil and groundwater contamination is remediated by natural microbial processes, without engineered amendment, to protect human health and the environment (Chapelle, 1999). A number of sites in the U.S. have been evaluated for this process (Wiedemeier et al., 1995), but its application in the colder groundwater conditions more commonly found in Canada has not been well addressed. The metabolic rate of the microorganisms active in bioremediation will directly influence the rate at which contaminants of concern are removed from the environment. It is generally accepted that microbial growth rates double with approximately every 10°C increase in temperature until an optimum temperature is reached (Prescott et al., 1993). More recent studies have suggested that microorganisms acclimated to cold temperatures may degrade contaminants at higher rates than predicted by applying this principle (Bradley and Chapelle, 1995; Margesin and Schinner, 1997b).

1.1 Hydrocarbon Contamination

It has been estimated that 25% of Canadians rely on groundwater for domestic use (Environment Canada, 1998). Accidental leaks and spills of petroleum products resulting from deteriorating storage tanks and poor fuel management practices have resulted in contamination of groundwater in many areas. Hydrocarbon contaminants are present at a significant portion of the sites requiring remediative efforts in North America. According to a recent estimate, there are approximately two million underground storage tanks in the U.S.A. and there have been over 300,000 confirmed releases into the subsurface (USEPA, 1998a). The most soluble hydrocarbons are considered depressants to the central nervous system and one compound, benzene, has been linked to leukemia in humans (Corseuil and Alvarez, 1996).

1.1.1 Nature of Subsurface Hydrocarbon Contamination

When hydrocarbons are released into the environment, they will migrate downwards through permeable unsaturated soil until either an impermeable layer or the water table is intercepted. Hydrocarbons are classed as light non-aqueous phase liquids (LNAPL) because

they are less dense than water. Due to this density contrast, migrating free product will pool on the water table before dissolving in the groundwater.

Hydrocarbons used for fuel are complex mixtures of a variety of inorganic and organic compounds. Table 1 lists the typical composition of crude oil, gasoline, and JP-4, a jet fuel. Each of these compounds has unique physical and chemical properties. While petroleum hydrocarbons as a whole are relatively insoluble in water, BTEX are the most soluble components (see Tables 2 & 3). These chemicals will preferentially dissolve in groundwater that comes in contact with LNAPL and will be transported from the initial spill area by a variety of mechanisms. The most dominant transport mechanism of the dissolved plume is generally due to the advective flow of the groundwater, but diffusion and dispersion also act to distribute dissolved contaminants in groundwater. Hydrocarbon migration in both the dissolved phase and the free phase will follow the path of least resistance resulting in preferential flow through coarser grained or fractured aquifer material. Mechanisms that retard the migration of BTEX in the subsurface include the adsorption of contaminant onto fine grained and organic material in the aquifer, volatilization, entrapment of free phase product as residual, and the biodegradation of contamination by microorganisms in the aquifer.

1.1.2 Remediation Alternatives

Traditional methods for the removal of hydrocarbon contamination from groundwater include pumping the contaminated groundwater for treatment at surface with activated carbon or air strippers. Another common approach for the treatment of contaminated soil is the excavation and treatment by an *ex situ* system. When used alone these methods can result in prohibitively long time periods for the removal of residual contamination and may be economically unfeasible. There may also be increased risk to potential receptors due to the handling requirements when the contaminant is brought to the surface and transported for *ex situ* remediation. Intrinsic bioremediation is an *in situ* treatment approach for contaminated soil and groundwater. *In situ* methods are often favoured over *ex situ* because they do not require the excavation of large quantities of earth, which can introduce a significant cost.

1.2 Intrinsic Bioremediation

The term natural attenuation has been used to describe the naturally occurring processes of dilution, dispersion, sorption, and biodegradation that cause contaminant concentrations to decrease when they are released in the environment. It has been shown (Wiedemeier et al., 1995) that given the right conditions, petroleum hydrocarbons can be biodegraded intrinsically before they migrate off site and pose a risk to a receptor (human, other animal, or plant). Intrinsic bioremediation refers to the microbial degradation of hydrocarbon contamination by the *in situ* microbial population without any engineered amendment (provision of nutrients, electron acceptors, etc.) (Chapelle, 1999). It should be emphasized that it is not a "do nothing" approach, as a considerable effort must be applied to successfully model and monitor a site.

The biodegradation process is best described by a series of oxidation-reduction reactions in which organic matter is the substrate, or food source, for microbes and acts as an electron donor (is oxidized). Various other compounds act as an electron acceptor (are reduced). The reaction is mediated by the microorganisms that gain the energy required for cell growth from the process. Of all oxidants, oxygen has the highest energy yield to microbes that utilize organic carbon as a food source (heterotrophs). As oxygen becomes depleted, other terminal electron acceptors (TEA's) are utilized, generally in the following sequence:

Dissolved Oxygen (DO) > Nitrate (NO_3) and Nitrite (NO_2) > Manganese (MnO_2) > Iron (III) (Fe^{3+}) >Sulfate (SO_4^{2-}) > Carbon Dioxide (CO_2)

Each successive TEA provides decreasing energy to microbes, which generally results in a sequentially lower rate of degradation of organic contaminants. As more contaminant is oxidized and TEA's are reduced, the redox potential in the groundwater decreases. This is illustrated in Figure 1.

1.2.1 Advantages and Limitations of the Intrinsic Bioemediation Approach

The intrinsic bioremediation methodology offers many advantages. Application of the intrinsic bioremediation protocol to over 40 sites in the United States cost between US$100,000 and US$175,000 per site and as such it is a comparatively inexpensive approach (Wiedemeier et

al., 1995). The required increment of effort beyond a typical site investigation is small and, given the right conditions, it is inherently safer than *ex situ* processes which require the transport and processing of toxic chemicals. Bioremediation can convert toxic organic contamination to relatively harmless reaction products such as CO_2, H_2O and N_2 gas, rather than simply concentrating the contamination in a different phase and creating a residual disposal problem. The *in situ* approach allows a site to be put to productive use while being cleaned up and generally requires less energy input and special equipment than *ex situ* approaches (USEPA, 1998b).

The *in situ* process requires more extensive investigation and monitoring than *ex situ* processes due to the heterogeneity of the natural environment. Less control of the remediation reaction process is afforded *in situ*, and therefore a more limited number of contaminants can be treated in this manner (Biggar, 1998a). Another limitation of intrinsic bioremediation is the potentially slow rate of the biodegradation reactions. If regulators require continuous monitoring of a contaminant plume, the long-term costs may be significant. If there is regulatory or economic pressure to remediate a site quickly, then an *ex situ* engineered remediation solution may be required to optimize the biodegradation process.

Hydrocarbon contamination contains a variety of compounds, often including BTEX. Each of these compounds has distinct characteristics in terms of rate and magnitude of dissolution in groundwater, which complicates modeling efforts. It has also been shown that most hydrocarbon-degrading microorganisms are able to degrade only one of several closely related compounds that make up the bulk of hydrocarbon contamination suggesting that a mixed microbial population may be necessary for complete degradation (Borden et al., 1994).

1.2.2 Optimal Environmental Conditions for Biodegradation

A number of criteria must be met for intrinsic biodegradation to serve as a viable remediation alternative. They are related to properties of the contaminant itself, the groundwater geochemical conditions, and the aquifer hydrogeology. Preferred conditions for viable sites include: minimal risk of contaminants coming into contact with receptors, low groundwater

velocities, and the presence of adequate nutrients, TEA's, and microbes. Some of the requirements are discussed in more detail below:

- The presence of hydrocarbon-degrading microorganisms;

This is rarely a limiting factor for BTEX degradation as there are many species of microorganisms capable of degrading BTEX that are found in many different environments (Borden et al., 1994).

- The chemical nature and biological availability of target pollutants;

Some organic molecules resist degradation due to their large size or type of functional groups or limited water solubility. Strong sorption on aquifer material can also hinder the ability of bacteria to attach to, absorb, or enzymatically attack the molecule (Godsy, 1994).

- The availability of electron acceptors;

As explained in detail in Section 2.1, appropriate compounds must be present that the microorganisms can reduce by the addition of electrons. This is the process by which the microorganisms obtain their energy.

- The availability of inorganic nutrients;

The major limiting elements for growth are nitrogen and phosphorus but sulfur, calcium, magnesium, and trace metals are also required and if not present in adequate supply will hinder cell growth.

- Adequate pH and temperature;

Near neutral pH values are usually optimum for the biodegradation of contaminant organic material. The effects of temperature on degradation are complex, but generally the rate of enzymatic degradation and bacterial metabolism double for every 10^0C increase.

- The relatively low concentration of toxic substances;

The presence of toxic substances, such as organic lead compounds present in gasoline, can limit microbial growth rates.

1.3 Overview of Thesis Report

This thesis presents an evaluation of intrinsic bioremediation of benzene, toluene, ethylbenzene, and xylenes (BTEX) at two separate sites at 4 Wing Cold Lake, Alberta. Cold Lake

is located near the 55th parallel in northeastern Alberta near the Saskatchewan border. By means of both field and laboratory investigations, the influence of temperature on the rate and extent of bioremediation was studied. The cold temperature study was completed as part of the site investigation for hydrocarbon contamination at the two sites.

Section 2 will discuss the current understanding of the mechanisms for biodegradation of hydrocarbon contamination and relevant concepts in chemistry and microbiology. Section 3 describes the overall program of investigation. Details of the unique investigation methodology, results and conclusions for each site are presented separately, in Sections 4 and 5. A discussion of the results of the laboratory microcosm study and what they indicate about the influence of temperature on biodegradation rate is included as Section 6. Section 7 addresses the unresolved questions which arose during the course of the investigation. A brief summary of the conclusions is included as the final section of this report.

Table 1: Typical Composition of Crude Oil (a), JP-4 (Jet Fuel) (b), and Gasoline (c)

(a) Components of Crude Oil (from Fetter, 1999)

Component	Concentration (% Volume)
Paraffins (Saturated Hydrocarbons)	25
Cycloparaffins	50
Aromatics	17
Asphaltics (>40 carbon atoms)	8

(b) Components of JP-4 (from Riser-Roberts, 1992)

Component	Concentration (% Volume)	Component	Concentration (% Volume)
C_5 hydrocarbons	3.9	C_9 aromatics	2.4
C_6 paraffins & cycloparaffins	10.2	C_{10} hydrocarbons	12.8
Benzene	0.3	Naphthalene	0.2
C_7 paraffins & cycloparaffins	16.5	C_{11} hydrocarbons	12.0
Toluene	0.7	C_{12} hydrocarbons	4.7
C_8 paraffins & cycloparaffins	17.5	C_{13} hydrocarbons	1.6
C_8 aromatics (incl. xylenes)	1.6	C_{14} hydrocarbons	0.2
C_9 paraffins & cycloparaffins	13.4	C_{15} hydrocarbons	0.1

(c) Components of premium grade unleaded gasoline (from Fetter, 1999)

Component	Concentration (% Volume)
By Compound	
Benzene	1.96
Toluene	20.25
Ethylbenzene	0.94
p and m-Xylene	2.60
o-Xylene	1.61
All other	72.64
By Class	
Aromatics	44.20
Paraffins	9.33
Olefins (unsaturated hydrocarbons)	46.47

Table 2: Reported Values of Aqueous Solubility and Soil Sorption Coefficient (K_{OC}) for Selected Hydrocarbons

Compound	Solubility (mg/L)	K_{oc} (L/Kg)	Source
Benzene	1750	39	1
Benzene	1780	79	2
Benzene	1800 @25°C	49	3
Toluene	535	135	1
Toluene	537	190	2
Toluene	520 @25°C	180	3
Ethyl benzene	152	95	1
Ethyl benzene	140	468	2
Ethyl benzene	187 @25°C	257	3
Xylenes	198	240	1
o-xylene	162	405	2
o-xylene	152 @20°C	129	3
p-xylene	198	357	2
p-xylene	200@25°C	204	3
Hexane	9.5 @25°C	-	3
Octane	0.88 @20°C	-	3
Naphthalene	31.7 @25°C	550	3

Source:

1..... ASTM, 1995. (No temperature stated)
2..... Wiedemeier et al., 1995. (No temperature stated)
3..... Montgomery, 1996.

Table 3: Measured Typical Dissolved Concentrations[1] (in Water) of Water Soluble Components Present at Equilibrium in JP-4 and Gasoline
(from Weidemeier et al., 1995)

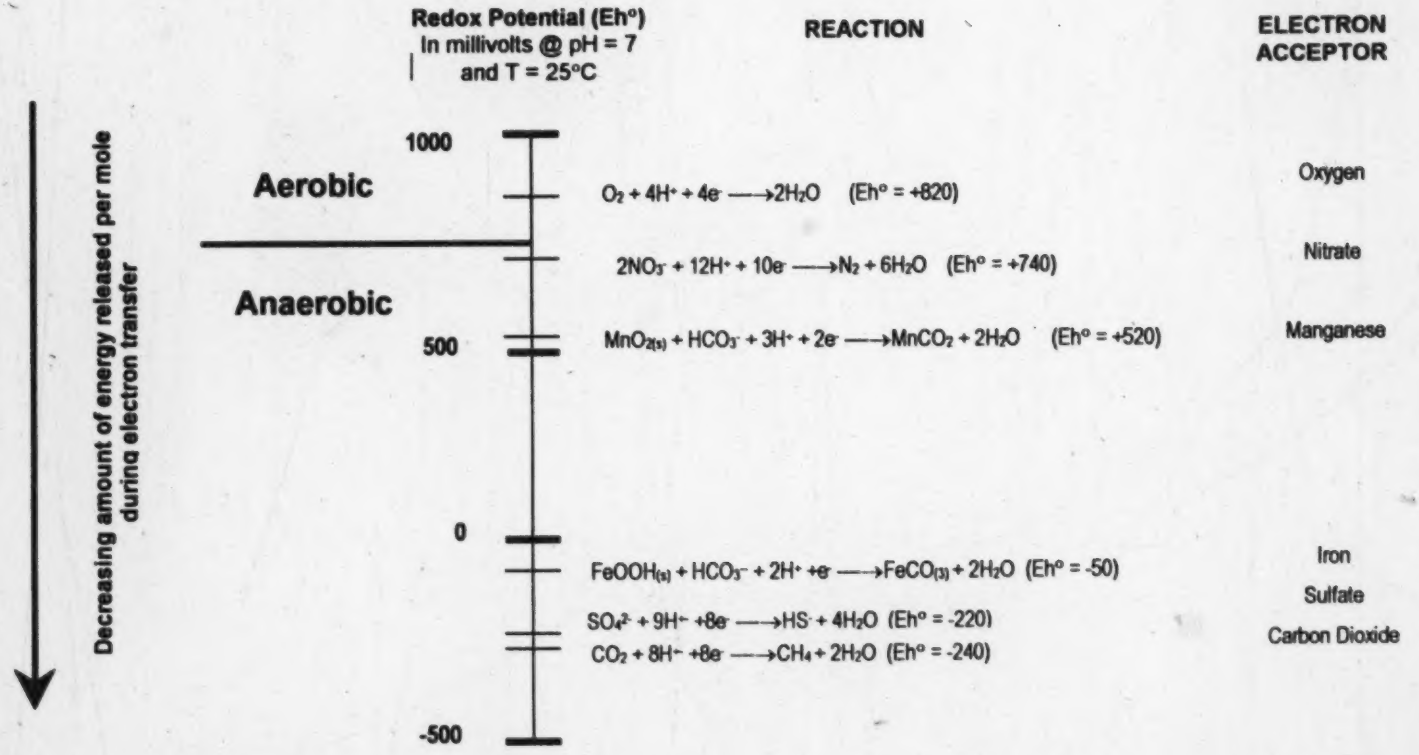
Compound	Gasoline Dissolved Concentration (mg/L)	Gasoline Dissolved Concentration (mg/L)	JP-4 Dissolved Concentration[2] (mg/L)
benzene	42.6	58.7	9.82
toluene	69.4	33.4	8.49
ethylbenzene	3.2	4.3	0.67
o-xylene	5.6	6.9	-
m- and p-xylene	11.4	15.4	-
xylenes	-	-	3.63
n-propylbenzene	0.4	-	-
3-,4-ethyltoluene	1.7	-	-
1,2,3-trimethylbenzene	0.7	-	-
1,2,4-trimethylbenzene	-	1.1	-
All Others	-	-	5.02
Total BTEX	132.2	118.7	22.61
Total Dissolved Concentration	135	119.8	27.63

Note:

1 at approximately room temperature
2 1:10 Fuel:Water ratio

Figure 1: Redox Potential for Various Electron Acceptors

(after Wiedemeier *et al.*, 1995)


Redox Potential (Eh°)
In millivolts @ pH = 7
and T = 25°C
REACTION
ELECTRON ACCEPTOR
Decreasing amount of energy released per mole during electron transfer
1000
Aerobic
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ (Eh° = +820)
Oxygen
$2NO_3^- + 12H^+ + 10e^- \longrightarrow N_2 + 6H_2O$ (Eh° = +740)
Nitrate
Anaerobic
500
$MnO_{2(s)} + HCO_3^- + 3H^+ + 2e^- \longrightarrow MnCO_2 + 2H_2O$ (Eh° = +520)
Manganese
0
$FeOOH_{(s)} + HCO_3^- + 2H^+ + e^- \longrightarrow FeCO_{3(s)} + 2H_2O$ (Eh° = -50)
Iron
$SO_4^{2-} + 9H^+ + 8e^- \longrightarrow HS^- + 4H_2O$ (Eh° = -220)
Sulfate
$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$ (Eh° = -240)
Carbon Dioxide
-500

2 LITERATURE REVIEW

This section presents a review of the current understanding of the microbiologically mediated processes by which hydrocarbons are degraded. Each significant TEAP will be discussed. The influence of temperature on chemical equilibrium, reaction kinetics, and microorganism behaviour will be also be addressed. A final note on previously reported investigations into the influence of temperature on biodegradation closes the section.

2.1 Biologically Mediated Hydrocarbon Degradation Processes

There are a variety of processes that have been shown to biologically degrade hydrocarbon contamination. Evidence for each mechanism has been gathered both from field studies examining the change in chemical species in the groundwater across a contaminated site and from laboratory studies under controlled environmental conditions.

2.1.1 Aerobic BTEX Degradation

Until the mid-1980's, it was thought that the only mechanism for hydrocarbon degradation was with oxygen as the terminal electron acceptor (Chapelle, 1999). Water saturated with air contains from 6 to 12 mg/L of dissolved O_2 (DO) depending on temperature and salinity. A major limitation to aerobic biodegradation in groundwater is the low solubility and limited recharge of oxygen (Borden and Bedient, 1986a). The extent of aerobic degradation is controlled by the amount of dissolved contaminant present, the rate of oxygen recharge, and the background oxygen content in the groundwater (Borden et al., 1994). Aerobic degradation of toluene can be represented stoichiometrically by the expression:

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O \qquad [1]$$

This relationship indicates that 9 moles of DO are required to degrade 1 mole of toluene. On a mass basis:

Mass toluene = 92 grams/mole x 1 mole = 92 grams

Mass oxygen = 32 grams/mole x 9 mole = 288 grams

The mass ratio of oxygen required to degrade one unit mass of toluene is therefore:

288:92 = 3.13:1

The mass ratio can also be calculated for benzene, ethylbenzene, and xylenes. By averaging the molecular weight of each component of BTEX, an average mass ratio is calculated to be 3.14:1 or 1:0.31. This means that for every milligram of DO consumed in Equation 1, approximately 0.3 mg of BTEX can be degraded. If it is assumed that there is no recharge of dissolved oxygen to a contaminated aquifer, that the microorganisms for aerobic biodegradation are present, and that the reaction runs to completion, the aerobic degradation of dissolved BTEX is therefore limited to 2 to 4 mg/L due to solubility limitations.

2.1.2 Degradation via Nitrate Reduction

Once dissolved oxygen has been depleted, denitrifiers can use nitrate as the terminal electron acceptor during BTEX degradation. Nitrate reduction has an energy yield comparable to that of aerobic degradation and the nitrate is reduced mainly to nitrogen gas. Most heterotrophic denitrifiers (organic carbon as food source, nitrate as TEA) found in aquifers are facultatively anaerobic which means the microbes can switch from utilizing molecular oxygen to using nitrate as a TEA (Kinzelbach and Schäfer, 1991). The degradation of hydrocarbons under denitrifying conditions has been well demonstrated both in laboratory experiments (Jørgensen et al., 1995) and based on field data (Hutchins et al., 1991). The complete degradation of toluene under denitrifying conditions can be represented by:

$$C_7H_8 + 7.2NO_3^- + 7.2H^+ \rightarrow 7CO_2 + 7.6H_2O + 3.6N_2 \qquad [2]$$

The average mass ratio of NO_3^- consumed to BTEX degraded is 4.9:1. In other words, for every milligram of nitrate reduced to N_2 in Equation 2, ideally 0.20mg of BTEX can be consumed, based on similar assumptions required in Section 2.1.1.

2.1.3 Degradation via Iron Reduction

Iron (III) (Fe^{3+}) is generally the most abundant potential electron acceptor for organic matter degradation in polluted aquifers because large amounts are present in the sediments of most aquifers {Borden, Gomez, et al. 1994 #2}. When dissolved oxygen and nitrate have been

depleted, microorganisms such as *Geobacter metallireducens* can use iron (III) as an electron acceptor to degrade hydrocarbons (Lovley, 1997). The most easily reduced forms of iron are amorphous and poorly crystalline Fe^{3+} hydroxides, oxyhydroxides, and oxides (Borden et al., 1994). The mineralization of toluene coupled to the reduction of ferric hydroxide can be represented by:

$$C_7H_8 + 36Fe(OH)_3 + 72H^+ \rightarrow 7CO_2 + 36Fe^{2+} + 94H_2O \quad [3]$$

The geochemical change most readily measured by groundwater monitoring in the field is the production of soluble iron (II) (Fe^{2+}). The average mass ratio of the metabolic by-product Fe^{2+} to total BTEX is 21.8:1. This means that for every milligram of Fe^{2+} produced in Equation 3, 0.05mg of BTEX can be consumed, based on the assumptions outlined in Section 2.1.1.

2.1.4 Degradation via Sulfate Reduction

It has been shown that BTEX can be degraded under sulfate-reducing conditions both in the laboratory (Beller et al., 1992; Edwards et al., 1992; Chapelle et al., 1996) and in the field (Davis et al., 1999). Sulfate is reduced to sulfide during the oxidation of BTEX. The process is not well quantified and the intermediates generated are not well understood (Wiedemeier et al., 1995). This process usually occurs near the centre of a plume, far from the surrounding uncontaminated (aerobic) groundwater (Corseuil and Alvarez, 1996). The reaction may be represented by the degradation of toluene:

$$C_7H_8 + 4.5SO_4^{2-} + 3H_2O \rightarrow 7HCO_3^- + 2.25H_2S + 2.25HS^+ + 0.25H^+ \quad [4]$$

The average mass ratio of sulfate consumed per mole of BTEX degraded is 4.7:1. For every milligram of sulfate consumed by Equation 4, 0.21mg of BTEX may be consumed, based on assumptions outlined in Section 2.1.1.

2.1.5 Methanogenic BTEX Degradation

An elevated level of dissolved methane gas in groundwater is evidence of methanogenic processes because methane does not usually occur in significant quantities in uncontaminated aquifers. Laboratory microcosm studies have demonstrated that BTEX could be degraded under methanogenic conditions (Grbic-Galic and Vogel, 1987; Wilson et al., 1986). The methanogens

themselves can only utilize simple molecules such as H_2, acetate, and CO_2. They rely on other species of microorganisms to break down more complex substrates to make them available to the methanogens. Generally, low rates of degradation are attributed to this mechanism. This may be due to the particular sensitivity of this type of microorganism to unfavorable environmental conditions including extreme pH and temperature levels and the presence of toxicants (Corseuil and Alvarez, 1996). A stoichiometric representation of the methanogenic degradation of toluene is:

$$C_7H_8 + 5H_2O \rightarrow 2.5CO_2 + 4.5CH_4 \qquad [5]$$

The average mass ratio of the metabolic by-product CH_4 to total BTEX is 0.78:1. This means that for every milligram of CH_4 produced in Equation 5, 1.28mg of BTEX can be consumed, based on the same assumptions stated in Section 2.1.1.

2.2 Influence of Temperature on Biodegradation

The process of biodegradation is complex and is intricately linked to both the chemical and the biological environment. As described below, cold temperatures can influence the extent of a chemical reaction, the rate at which a reaction progresses, and the metabolic functions of microorganisms. Recent research has examined the influence of temperature on the feasibility of biodegradation in lab and field-scale investigations.

2.2.1 Influence of Temperature on Chemical Equilibrium Constant

The equilibrium constant, K, describes the ratio of concentration of products to concentration of reactants for a given chemical reaction at a given set of standard conditions. For the reactions described by Equations 1 through 5 in Section 2.1, the equilibrium constant for each reaction represents the extent of biodegradation achievable under standard conditions. Temperature has a significant influence on the chemical equilibrium constant as described by van't Hoff equation. The van't Hoff equation can be written as (Çengel and Boles, 1998):

$$\frac{d(\ln K)}{dT} = \frac{\Delta H(T)}{RT^2} \qquad [6]$$

where: $d(\ln K)/dT$ = change in natural log of the equilibrium constant with temperature for an ideal gas

$\Delta H(T)$ = Change in Enthalpy at temperature, T (K)

R = the universal gas constant, 8.314 J mole^{-1} K^{-1}

For small temperature intervals, the enthalpy of reaction can be considered constant and the equation can be integrated to yield:

$$\ln \frac{K_2}{K_1} \cong \frac{\overline{h_R}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad [7]$$

where: $\overline{h_R}$ = enthalpy of the reaction

K_1 = equilibrium constant at temperature, T_1

K_2 = equilibrium constant at temperature, T_2

The relationship in Equation 7 indicates that as T_2 becomes larger, the equilibrium constant K_2 becomes larger. This shows that a reaction will move more towards completion and use up more reactants to generate more products at a higher temperature.

2.2.2 Influence of Temperature on Reaction Kinetics

Temperature also has a significant effect on the kinetic rate of reaction as described by the Arrhenius equation. The Arrhenius equation can be written (Sawyer et al., 1994):

$$\frac{d(\ln k)}{dT} = \frac{E_a}{RT^2} \qquad [8]$$

where: $d(\ln k)/dT$ = change in natural log of a reaction rate constant with temperature

E_a = activation energy, J mole^{-1}

T = absolute temperature, K

This equation can be integrated and expressed as (Chapra, 1997):

$$k(T) = Ae^{\frac{-E_a}{RT}} \qquad [9]$$

where: A = a preexponential or frequency factor

$k(T)$ = rate constant at Temperature, T

$$\frac{k(T_2)}{k(T_1)} = e^{\frac{E_a(T_2-T_1)}{RT_2T_1}} \quad [10]$$

Because the temperatures of most reactions of interest vary over a narrow range, the product of T_1 and T_2 can be considered relatively constant. As a consequence, the following constant can be defined:

$$\theta = e^{\frac{E_a}{RT_2T_1}} \quad [11]$$

then, the ratio of rates can be expressed as:

$$\frac{k(T_2)}{k(T_1)} = \theta^{T_2-T_1} \quad [12]$$

Since many reactions are reported at 20°C, the above equation is often expressed as:

$$k_T = k_{20}\theta^{(T-20)} \quad [13]$$

Typical values of θ for a variety of reactions are included in Table 4.

2.2.3 Influence of Temperature on Microorganism Behaviour

Microorganisms are particularly sensitive to temperature because they are usually unicellular and their internal temperature varies with the surrounding environment (Prescott et al., 1993). Based on their optimum growth temperatures, microorganisms are classified as psychrophiles, psychrotrophs, mesophiles, or thermophiles (Prescott et al., 1993). Psychrophiles have optimum temperatures for growth of approximately 15°C while psychrotrophs can grow at 0°C despite optima between 20 and 30°C. These two classes of microbes are considered primarily responsible for cold temperature bioremediation. Most microbes are mesophiles, growing most rapidly at temperatures between 20° and 45°C and a temperature minimum of approximately 15-20°C. Thermophiles experience optimum growth at temperatures above 45°C.

The upper temperature limits for microorganism survival are likely caused by the denaturation of proteins and the breakdown of cell membranes overwhelming the increased rate of enzyme-catalyzed reactions (Gaudy and Gaudy, 1980). At low temperatures, the fluidity of a cell membrane may be decreased sufficiently to prevent the functioning of transport systems,

possibly inhibiting substrates from entering the cell rapidly enough to support cell growth. Temperatures below the minimum for cell growth are not normally lethal, and thus affect the growth rate but not the viability of the microorganism (Gaudy and Gaudy, 1980).

2.2.4 Influence of Temperature on Biologically Mediated Reactions

The temperature dependence of biologically mediated reactions is often expressed by the quantity Q_{10}, which is defined by the ratio of the reaction rate at a particular temperature to the rate at 10°C lower (Chapra, 1997):

$$Q_{10} = k\,(20^{0}C)/k\,(10^{0}C) \qquad [14]$$

This can be related to the factor θ (described in Section 2.2.2) by substitution, yielding:

$$Q_{10} = \theta^{10} \qquad [15]$$

It can then be calculated that for a doubling of the reaction rate at a temperature increase from 10°C to 20°C, the Q_{10} factor will equal 2, and θ will equal 1.072. A summary of commonly used values for the temperature dependant constants Q_{10} and θ is included as Table 4.

2.2.5 Previous Investigations into Temperature Influence on Biodegradation

Generally, rates of enzymatic degradation and bacterial metabolism are expected to double for every 10°C increase in temperature until inhibitory temperatures are reached (often 40-50°C) (Godsy, 1994). The influence of temperature on bioremediation is complex, as it can change the contaminant physical properties, its bioavailability, and its toxicity to microorganisms (Godsy, 1994).

The slow rate of microbial activity at cold temperatures has been thought to be responsible for the low biodegradation rates encountered in some studies. Braddock and McCarthy (1996) suggest that a short annual thaw season was responsible for limited microbial processes at a hydrocarbon contaminated site in Alaska. They noted, however, that mineralization rates interpreted from a microcosm study were comparable to more temperate systems. Sparrow and Sparrow (1989) examined an experimental oil spill site in interior Alaska 10 years following contamination, and it was discovered that substantial amounts of petroleum residues remained in soil samples. Tumeo and Gawde (1997) suggested this was due to the low

10 years following contamination, and it was discovered that substantial amounts of petroleum residues remained in soil samples. Tumeo and Gawde (1997) suggested this was due to the low temperatures and lack of available water, but the authors of the original study made no such claim. It is likely that the heavier fraction of crude oil which is more resistant to degradation than lighter molecular weight organic molecules was the dominant remaining contamination. Corseuil and Weber (1994) performed batch experiments with o-xylene at 8°, 22°C and 29°C. They modeled the data with modified Monod kinetics and determined that the maximum substrate utilization rate decreased by a factor of three for an approximately 10°C decrease in temperature ($Q_{10} = 3$).

Three field studies on bioventing reported the influence of temperature on the rate of bioremediation. In one study in Alaska, it was reported that the rate of biodegradation attained in the test plots were temperature dependent, and could be roughly approximated by an Arrhenius relationship (Sayles et al., 1995). Results from another investigation in west central Alberta suggest that cold *in situ* temperatures (5-8^{0}C) did not inhibit the rate of bioremediation (Moore et al., 1995). Both studies indicated that significant rates of bioremediation occurred without engineered amendment (i.e., in control plot or with blower equipment shut off) at the cold *in situ* temperature. The microbial respiration rate in a full-scale bioventing system in northern Alaska was investigated and was loosely correlated to the *in situ* temperature variation (Simpkin et al., 1995).

Laboratory batch-type experiments have shown that the extent of mineralization of diesel hydrocarbon contamination by cold-adapted microorganisms at 10^{0}C was similar to that reached at higher incubation temperatures (Margesin and Schinner, 1997a; Margesin and Schinner, 1997b). The same investigators showed that indigenous microorganisms could degrade a water sample contaminated with fuel oil and anionic surfactants at 10^{0}C with the addition of inorganic nutrients (Margesin and Schinner, 1998).

Findings from one laboratory microcosm study indicate that the adaptation of the *in situ* microbial community to cold temperatures may permit higher rates of biodegradation than otherwise anticipated (Bradley and Chapelle, 1995). The authors concluded that it was not

appropriate to estimate rates of hydrocarbon degradation at cold temperatures based on the temperature response of microorganisms acclimated to warmer environments.

This review of recent research in cold temperature bioremediation indicates that the biodegradation of BTEX may occur at rates faster than predicted by a Q_{10} approximation. The investigation of the relationship between biodegradation rate and temperature is complicated however by the nature of the physical environment (Braddock and McCarthy, 1996) and the nature of the contaminant (Sparrow and Sparrow, 1989). The difficulty in relating laboratory microcosm studies (Bradley and Chapelle, 1995; Margesin and Schinner, 1997a, 1997b; Corseuil and Weber, 1994) to results from field investigations (Sayles et al., Moore et al., 1995; Simpkin et al., 1995) suggests that further study of cold temperature bioremediation is warranted.

Table 4: Typical Arrhenius and Q_{10} Constants for Various Reactions

Reaction	Q_{10}	θ	Temperature Range ^{0}C	Source
Activated Sludge		1.00-1.08		1
Aerated lagoons		1.04-1.10		1
Activated Sludge Decomposition	2.85		10-20	2
Activated Sludge Decomposition	2.22		15-25	2
Activated Sludge Decomposition	1.89		20-30	2
Anaerobic Sludge Decomposition	1.67		10-20	2
Anaerobic Sludge Decomposition	1.73		15-25	2
Anaerobic Sludge Decomposition	1.67		20-30	2
Anaerobic Sludge Decomposition	1.48		25-35	2
Anaerobic Sludge Decomposition	1.0		30-40	2
BOD decomposition	1.58	1.047	≈20	3
Phytoplankton growth	1.89	1.066	≈20	3

Source:

1. Tchobanoglous and Burton, 1991
2. Sawyer et al., 1994
3. Chapra, 1997

3 PROGRAM OF INVESTIGATION

Wiedemeier et al. (1995) developed a protocol for implementing intrinsic bioremediation for sites contaminated with dissolved fuel compounds in groundwater that has provided the framework for this investigation. Important elements of an assessment include: development of a preliminary conceptual model, investigation of stratigraphy and groundwater characteristics, contaminant and geochemical sampling, conceptual model refinement, simulation of intrinsic bioremediation using solute fate and transport modeling, exposure pathways analysis, and development of a long term monitoring plan. The protocol outlines a process whereby different lines of evidence are gathered to show that biodegradation processes are occurring. In particular, the report suggests that the lines of evidence include:

1) Documented loss of contaminants at the field scale,

2) Contaminant and geochemical analytical data, and

3) Direct microbial evidence.

Arguably the most important component of a site investigation in support of intrinsic bioremediation is the groundwater and soil sampling approach. The documentation of contaminant and geochemical trends depends on the adequate characterization of the contaminated aquifer.

Direct microbial evidence can be used to show that indigenous microorganisms are capable of degrading contaminants of concern. Microbial enumeration techniques can indicate the dominant type of microorganisms present, and confirm the presence of contaminant degrading species.

Computer models of the fate and transport of contaminants can only be as accurate as the information entered into the model, and thus rely heavily on a meaningful site characterization. A wide variety of models of varying levels of complexity exist, each with their own merits. The successful computer modeling effort can be used to predict the future extent of dissolved contamination, to assess the potential for contaminant exposure to downgradient

receptors, and to convey the scope of the contamination to non-technical personnel (Wiedemeier et al., 1995).

3.1 Groundwater and Soil Sampling for Hydrocarbon Contamination

Since decisions regarding the significance of contamination and the extent of cleanup have far-reaching effects, it is essential that they be based on accurate measurements of the contaminant distribution at the field site. This can be difficult to achieve as the sampling process is subject to numerous sources of random and systematic errors (Siegrist and Jenssen, 1990). The sampling approach selected depends on the overall objectives of the investigation. A multi-phased approach to an investigation permits the most effective use of resources. Preliminary non-intrusive or low cost and low precision investigations can been carried out to delineate a contaminant plume and identify the expected type of contamination. More precise follow-on investigations can then be carried out to refine the site characterization.

Sample collection and handling activities can contribute relatively large errors compared to the analysis itself. This is particularly true of the volatile organic compounds (VOC's) associated with hydrocarbon contamination. The high vapour pressure and high Henry's constant for these compounds indicate that they will readily partition to the atmosphere (Sawyer et al., 1994). Volatile organic compounds which exhibit these characteristics are among the most frequently encountered contaminants at hazardous waste sites (Hewitt et al., 1992).

The accurate and representative sampling of organic compounds is a vital component to remedial site characterization. There are a variety of different methods to sample different environmental media, each with inherent limitations. The choice of method often depends on the limitations of the site, the expected amount and type of contamination, relative cost of the investigative methods, and the level of accuracy required.

3.1.1 Sampling Approach

Discrete samples at a site provide information that is often extrapolated to include the whole area under investigation. While the focus of errors in most sampling and analysis projects is on laboratory and data-handling sources, sampling bias can result in much larger errors than

those associated with analyses (CCME, 1993). There are a number of different approaches to representative sampling. Systematic sampling is preferable to facilitate geostatistical data analysis, but judgmental and random sampling may achieve greater accuracy within specific areas of interest (CCME, 1993). A tabular comparison of sampling approaches is presented below.

Basic Sampling Approaches (from CCME, 1993)

Approach	Relative # Samples	Relative Bias	Basis of selecting sample locations
Judgmental	Smallest	Largest	Prior history/ technical judgement
Systematic	Larger	Smaller	Consistent grid or pattern
Random	Largest	Smallest	Simple Random Selection

3.1.2 Analytical Quality Control

There are many different quality control (QC) methods useful in sampling programs. The selection of the type of QC sample depends on the data quality objectives of the site being investigated. *Field blanks* and *rinsate blanks* are used to measure sampling bias, determine the limit of detection in the field and provide assurance of successful decontamination procedures (Italicized terms are defined in the List of Nomenclature and Abbreviations). *Replicates, laboratory blanks* and *standard reference samples* are used in the laboratory to determine analytical errors (USEPA, 1991).

3.1.3 Groundwater Monitoring Well Construction

Groundwater monitoring wells facilitate discrete groundwater samples to assess the concentration of dissolved contaminants and to investigate the potential for free product. Certain practices relating to the construction of a groundwater monitoring well can significantly influence the sample quality. The selection of proper well design and its construction and development are critical for collection of groundwater samples that are representative of the quality of water in the aquifer (Church and Granato, 1996). The construction materials must be chemically inert and not influence the contaminants of interest. Screen materials such as polyvinylchloride (PVC),

stainless steel, and Teflon® each have their own merits in terms of strength, chemical properties, and cost (Byrnes, 1994).

Monitoring wells screened over a large interval provide a better hydrologic connection to the aquifer at a lower cost than multiple short-screened wells. However, bias in groundwater data may be caused by vertical flow in long-screen wells that straddle heterogeneous layers in the subsurface. It has been shown that even in relatively homogeneous unconfined sand and gravel aquifers the use of long screen wells does not provide representative water quality samples and that vertical flow in these wells can transport contaminants to pristine zones of an aquifer (Church and Granato, 1996).

When a well is installed using an auger rig it is common for clayey soils to smear along the walls of the borehole. Similarly, when mud rotary drilling techniques are employed, a mudcake can develop along the walls of the borehole. These occurrences inhibit the flow of groundwater into a well and can affect the geochemical equilibrium. To overcome this problem, a monitoring well must be "developed". Development removes sediment from inside the monitoring well casing and flushes fine grained sediments from the formation immediately adjacent to the screened interval. This is accomplished by pumping large volumes of water out of the well through a surge block that can be raised and lowered in the borehole.

3.1.4 Groundwater Sampling for Chemical Analysis

The practice of sampling water from a well also involves important considerations in both the method and the device used to obtain the sample. Water samples are in a chemically dynamic state and the moment they are removed from the sample site, chemical, biological, and physical processes that change their compositions may commence (CCME, 1993). VOC's are continuously lost to the atmosphere during sampling at a rate directly proportional to the Henry's constant for the compound. In many sampling situations the groundwater is highly charged with gases such as methane and carbon dioxide. When the groundwater sample is removed and lowered to atmospheric pressure, these gases exsolve creating bubbles or headspace into which VOC's can partition (Barker and Dickhout, 1988). As a result of this phenomenon, the ability of the sampling device to prevent losses of these gases to the atmosphere can significantly affect

the measured volatile organic concentrations. Comparisons of sampling pumps have revealed that systematic errors related to the sampling mechanism can reduce the accuracy of monitoring data by factors of two to three times that involved in analytical procedures (Barcelona et al., 1984). Experimental results indicate that while most pumping mechanisms perform satisfactorily for well purging and the measurement of solution parameters, the sampling of gas-sensitive and volatile chemical constituents can be significantly biased by degassing and loss of volatiles during sampling (Barcelona et al., 1984). Further research has suggested that the use of suction lift pumps increased volatilization during sampling when compared to bladder pumps and momentum lift pumps (Barker and Dickhout, 1988). As a result, groundwater monitoring wells sampled for VOC analysis should be obtained with bladder or momentum lift pumps to minimize losses during sampling.

3.1.5 Soil Sampling for Chemical Analysis

Samples to be analyzed for VOC's require minimal disturbance, and methods involving augering into the soil may be inappropriate (Byrnes, 1994). Split tube and solid tube samplers can be used to collect either grab or composite samples and are effective tools for all types of potential contaminants provided soil disturbance during handling is minimized.

There are currently no industry-wide standardized procedures for sampling soils for VOC analyses that are consistently applied. In the United States, disturbed soil samples are often stored in Teflon-sealed glass jars and refrigerated at 4^0C. Simple procedures such as these may lead to substantial error when sampling soils for VOC's (Siegrist and Jenssen, 1990; Hewitt, 1994a; Hewitt, 1994c). The soil may be fractured and expose additional surface area permitting the release of weakly sorbed and physically trapped volatile organics. Techniques to address these losses are under development (Hewitt, 1994a; Hewitt, 1994b), but their application may reduce the representativeness of a sample if smaller discrete samples are analyzed (Biggar, 1998a). One method of reducing volatile losses is to analyze soil in the field immediately after sampling, or to transport samples to the laboratory for analysis without delay.

Losses due to biodegradation of the organic content in the soil sample between the time of sampling and analysis have also been found to be significant. A common technique is to

preserve soil samples at a temperature of 4°C for a maximum period of 14 days (Hewitt, 1994a). Experimental evidence indicates that this may be inadequate for a number of chemical constituents and that the use of a chemical preservative may better prevent losses due to biodegradation (Hewitt, 1994a).

3.2 Microbiological Investigation Methodology

An understanding of the microbial community and its influence is fundamental to understanding the degradation of hydrocarbon contamination at a site. In particular, an investigation of the microbial community can yield valuable information when attempting to document intrinsic bioremediation (Braddock and McCarthy, 1996).

Enumeration of the microbial community can provide supporting evidence for the dominant TEAPs and can confirm the presence of hydrocarbon-degrading microorganisms. Microcosm studies utilizing indigenous microorganisms and soil and groundwater from a site can provide convincing documentation of the occurrence of intrinsic bioremediation (Wiedemeier et al., 1995).

3.2.1 Microbial Enumeration

The most probable number (Colwell, 1979) technique, also known as dilution to extinction, has been applied extensively in the study of microorganisms (Colwell, 1979). It offers a relatively simple means for assessing the number and type of microorganisms present in soil and water, and has been used routinely in the water and wastewater treatment field (Tchobanoglous and Burton, 1991). More recently it has been applied in the assessment of contaminated sites, including cold temperature investigations (Braddock et al., 1999; Margesin and Schinner, 1997a; Margesin and Schinner, 1997b).

3.2.2 Microbial Activity

Microcosm studies can provide direct evidence of the occurrence of biodegradation and a means of estimating its rate. A reliable estimate for the biodegradation rate at a contaminated site is an important step in assessing the application of intrinsic bioremediation (Chapelle et al 1996). As outlined in Section 2.1, a laboratory study under strictly controlled conditions can be

used to demonstrate biodegradation under a variety of environmental conditions. These studies can be conducted either by directly monitoring the change in concentration of a contaminant of interest (Kelly et al., 1996; Corseuil and Weber, 1994), or by utilizing a radiolabelled contaminant and measuring the biodegraded product (Fedorak et al., 1982; Brown et al., 1991). They also can be used to comparatively investigate the treatment of samples with nutrients and fertilizers.

The delay, or lag time, occurring before the metabolism of contamination, and the extent of conversion of contamination can also be interpreted and lead to a greater understanding of the microbial system (Stapleton and Sayler, 1998).

Biodegradation rate constants determined by microcosm studies are often much greater than rates interpreted from field evidence, and as such may best be used as indicators of the potential for intrinsic bioremediation (Wiedemeier et al., 1995). Hydrocarbon degradation rates measured in aerobic or denitrifying microcosm environments may not adequately represent field conditions as field biodegradation rates may be limited by the delivery of electron acceptor to the subsurface environment and not by the microbial activity (Wiedemeier et al., 1995; Borden and Bedient, 1986a). In addition, the dominant degradation mechanisms may be a different TEAP. In this investigation, the rates of biodegradation for different incubation conditions are compared with each other to investigate the influence of temperature on biodegradation rate.

3.3 Computer Modeling Applications for Intrinsic Bioremediation

Contaminant fate and transport modeling is an important component of intrinsic bioremediation assessment. It employs site-specific data to simulate and predict contaminant concentration levels and migration pathways. A wide range of levels of modeling sophistication are available, from straightforward analytical models such as BIOSCREEN (Newell et al., 1997) to more complex numerical models such BIOPLUME (Rifai et al., 1987).

BIOSCREEN is a non-proprietary software package available for distribution through the USEPA. The model accounts for the processes of advection, dispersion, adsorption and biodegradation to predict contaminant transport. Designed as a preliminary screening tool, it has been used effectively to evaluate natural attenuation of hydrocarbon contamination (Wilson et al.

1999). At large, complex sites, a more sophisticated model is probably more appropriate, but at less complicated, lower-effort sites such as service stations, BIOSCREEN may be adequate (Newell et al., 1997).

BIOPLUME II is a well documented, readily available numerical model that has been used extensively to predict the fate and transportation of hydrocarbon contamination (Borden and Bedient, 1986b; Rifai et al., 1988; Wiedemeier et al., 1995). This model provides a two-dimensional solute transport solution and assumes that the hydrocarbon compounds are degraded in an instantaneous reaction with available dissolved oxygen. Anaerobic decay is simulated by applying a first-order degradation rate (Rifai et al., 1987).

4 FIRE FIGHTER TRAINING AREA[1]

A study was performed at the 4 Wing fire fighter training area (FFTA) to evaluate the viability of intrinsic bioremediation as a method of remediation. The study area is situated near the centre of the air force base about 250m north of the main airfield runway. Subsurface contamination has resulted from infiltration of hydrocarbons (dominantly jet fuel) used to ignite controlled fire burns of a jet mock-up within a bermed area. Fire fighter training has been ongoing since 1955. Contaminated soil from the source area was excavated and landfarmed in 1996 leaving a pit approximately 50mx70mx4m deep (see Figure 2 for site map). Numerous investigations to delineate the contaminant plume have been carried out by a number of different consultants, but site closure issues remain unresolved.

4.1 Scope of Work

The investigation at this site sought to resolve the location of the contaminant plume and investigate the potential for intrinsic bioremediation of the dissolved contaminants of concern.

The removal of the bulk of the contaminant source combined with the relatively low groundwater velocities across the site suggested that the mobilization of contamination off the site was low risk. The FFTA has likely contained subsurface contamination for decades and significant levels have not been detected beyond 100m downgradient.

A significant amount of work had been carried out at the FFTA prior to this investigation, providing extensive information for preliminary site characterization. The presence of a number

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[1] A version of this chapter has been published in two conference papers.

Johns, C.A., Biggar, K.W., Foght, J., Mullick, A., 1999. Intrinsic Bioremediation of BTEX in a Cold Temperature Environment. Proceedings of the Assessment and Remediation of Contaminated Sites in Arctic and Cold Climates (ARCSACC), Edmonton, Alberta, May 3-4, 1999. pp. 111-118.

Johns, C.A., Biggar, K.W., Foght, J., Mullick, A., 1999. Intrinsic Bioremediation of BTEX in a Cold Temperature Environment. Proceedings of the International Symposium on In Situ and On Site Bioremediation, San Diego, CA, April 19-22, 1999. Vol 1: 195-200.

of monitoring wells provided access to groundwater samples that were analyzed to indicate the concentrations of contaminants and TEAs upgradient, within the contaminant plume, and downgradient. The installation of a monitoring well within the plume during this investigation was necessary for hydrogeological testing in a well with known characteristics and dimensions. Direct push technology was utilized for groundwater sampling (HydroPunch®) in two transects downgradient of the source area. Hollow and solid stem soil coring permitted assessment of stratigraphy and chemical analysis of selected soil samples. The microbial community was characterized by analyzing a soil sample from within the contaminant plume. The groundwater temperatures at 4 Wing are colder than those sites where intrinsic bioremediation has been documented in the literature. Because the rate of bioactivity is highly temperature dependent, laboratory tests on the microbial activity were performed at the average *in situ* temperature (8°C). This temperature was determined based on over 20 measurements at both sites in October 1998.

4.2 Previous Studies

Dames & Moore submitted a report in January 1994 detailing a site investigation carried out in 1992 as part of a series of environmental site assessments of FFTAs at various Canadian Forces Bases. A geophysical survey (Electromagnetic) was carried out and ten boreholes were drilled with monitoring wells installed at each location. Selected soil and groundwater samples were analyzed for organic contamination revealing elevated levels of BTEX, which is typical of hydrocarbon contamination. BTEX contamination appeared to be confined to the training area, although a limited downgradient subsurface investigation was initiated. Investigators suggested the existence of two separate aquifers: a shallow unconfined aquifer that appeared to flow to the northeast, and a deeper aquifer, separated by a clay till horizon. The lower aquifer appeared to be flowing locally towards a groundwater low in the centre of the training area, and then to the northeast. Recommendations from the report included the excavation and landfarm treatment of the contaminated soil (Dames & Moore, 1994).

A report submitted by HBT Agra in February 1994 outlines the installation of four monitoring wells east of the FFTA. Soil hydrocarbon vapours were measured and one soil

sample was analyzed for hydrocarbon contamination. Groundwater samples were analyzed from each well for Total Petroleum Hydrocarbon (TPH) contamination and one sample was tested for BTEX, lead, and phenols. No contamination was detected (HBT AGRA Limited, 1994).

In 1996, excavation of the contaminated soil and subsequent landfarming treatment resulted in an open pit approximately 4m deep and 50x70m in lateral extent. Four drill holes eight to eleven metres deep were advanced adjacent to the excavation in September 1996. Borehole logs submitted by Agra E&E Ltd. note that trace hydrocarbon odours were observed in soil at the water table below the clay just south of the pit.

EBA Engineering consultants submitted a report in March 1998 detailing 16 boreholes with two monitoring wells installed within 10-15m of the south and east excavation boundary. Elevated soil hydrocarbon vapours were detected at each borehole location with the exception of one hole at the northeast corner. Nine soil samples and two groundwater samples were analyzed for hydrocarbon contamination. Elevated levels of BTEX, Total Volatile Hydrocarbons (TVH), and TPH were detected both in soil and groundwater samples (EBA Engineering Consultants Ltd, 1998).

Review of the information in these reports provided an understanding of the site stratigraphy and hydrogeology, and an indication of the extent of soil and groundwater contamination at the time of the studies.

4.3 Investigation Methodology

This section of the report describes the work performed in the field. The results of sample analysis and field tests are discussed in detail in subsequent sections.

Sampling investigations were initiated on three separate occasions. The initial site reconnaissance and groundwater sampling of selected existing monitoring wells was carried out in June 1998. Groundwater table elevations were measured and the presence of hydrocarbon odour or free product was recorded for all remaining wells. In August 1998, an auger drill rig equipped with hollow stem augers and direct push water sampling capability was utilized. One monitoring well was installed and four HydroPunch® holes were advanced for groundwater

sampling. Two existing monitoring wells were sampled for contamination and geochemistry. A site visit in October 1998 permitted five more HydroPunch® holes to be advanced, two more monitoring wells to be sampled, a final round of water table elevations to be recorded, a soil sample for laboratory biodegradation microcosm analysis to be obtained, and hydrogeological testing to be carried out. Borehole logs for the monitoring well (MW-01) and the auger hole (AH-21) are included in Appendix A.

4.3.1 Sampling Program

Samples of vapour, soils, and groundwater were taken upgradient, within the contaminated source area, and downgradient. These samples were required to delineate contamination, to demonstrate TEA utilization, and to conduct microbial analysis. The site was sampled in sequence from areas of least contamination towards the source area. Quality assurance techniques were applied through the use of *rinsate blanks* and *replicate* groundwater samples as discussed in Section 4.6.2.

4.3.1.1 Soil Vapour Sampling Method

Lower explosive limit (LEL) levels provide an indication of the extent of hydrocarbon contamination in a soil sample. Selected soil samples were retrieved from the split-spoon and sealed in a plastic sampling bag. Readings were taken with a gas detector by inserting the sampling tube into the bag once equilibrium conditions were reached (5-10 minutes).

4.3.1.2 Soil Sampling Method

Soil samples for organic analysis were obtained using a hollow stem auger and an unlined 8.6cm (3-3/8") diameter split-spoon sampler. The continuous hollow stem coring of the soil reduced sample disturbance and thus permitted both better delineation of stratigraphy and better soil sample quality for chemical analysis than solid stem coring could provide. The cores were inspected and described according to the Unified Soil Classification System (Borehole logs are included as Appendix A). For chemical analysis, subsamples of intact clumps of soil were

placed into 250mL glass jars with minimal headspace and immediately sealed with Teflon®-lined screw top lids.

All sampling equipment was rinsed with methanol and de-ionized water between sampling intervals. Potentially contaminated drilling equipment was cleaned with high-pressure steam and detergent between boreholes. Soil samples for chemical analysis were stored no longer than 10 days, in the dark, at approximately 4°C until analyzed at Enviro-Test Laboratories (ETL), Edmonton.

4.3.1.3 Groundwater Sampling Method

Groundwater samples were analyzed for the presence of hydrocarbons (each component of BTEX, volatile and extractable hydrocarbons), terminal electron acceptors (dissolved oxygen (DO), nitrate, nitrite, sulfate), biodegradation by-products (sulfide, methane and iron (II)), pH, electrical conductivity, redox potential, and temperature.

A Well Wizard pneumatic bladder pump was used to sample the monitoring wells and the "micropurging" technique was implemented (API Soil and Groundwater Technical Task Force, 1998). This low flowrate, positive displacement pump efficiently provided representative groundwater samples while minimizing loss of volatile contaminants or aeration and oxidation of geochemical constituents. In this process, water was slowly pumped from the formation (~600ml/min) into a flow-through cell containing probes that measured the pH and redox (Oakton®: WD-35615), DO (Lamotte®: DO 4000), electrical conductivity (Oakton®: WD-35607), and temperature (all probe types). When these parameters stabilized it was assumed that formation water was being withdrawn rather than "stale" water which may have remained in the well screen. Water was gently poured down the side of sample vials so as not to agitate or create bubbles, which could strip gases dissolved in the water.

The pump and flow-through cell was disassembled, cleaned and rinsed with distilled water after every well was sampled. Periodically after cleaning, distilled water was flushed through the entire pump system and a *rinsate* sample analyzed to confirm that it was not contaminated.

Water samples were obtained from the HydroPunch® holes in the following manner: the sampler (Figure 3) was driven to the depth of interest, the outer casing withdrawn 0.45m (18") exposing the stainless steel screen, and water allowed to flow into the screen and up the push rod. Water sampling was then accomplished using a Waterra® pump connected to a 1.3cm (0.5") diameter Teflon®-lined tube inside the push rods. HydroPunch® holes were backfilled with bentonite chips to seal off potential connections between the upper and lower aquifers.

Groundwater samples were preserved in separate containers as listed in Table 5, and stored no longer than 10 days, in the dark, and at approximately 4°C until analyzed. Analysis for hydrocarbons, nitrate, nitrite, sulfate, sulfide and iron (II) were carried out at ETL, Edmonton. Methane analysis was performed at the University of Alberta. Field measurements of pH, electrical conductivity, dissolved oxygen, redox potential and temperature were obtained by calibrated hand-held meters in a flow-through cell.

4.3.1.4 Soil and Groundwater Sample Analysis

A more detailed account of the analytical methods employed by Enviro-Test Laboratories for all chemical analysis is included as Appendix E. Briefly, volatile organic contaminants were measured with an automated headspace gas chromatographic/ mass spectrometric analysis technique. Metals were analyzed by inductively coupled plasma spectrophotometry, and other inorganics by ion chromatography.

Groundwater methane concentration was measured by gas chromatographic (Kampbell and Wilson, 1989) headspace analysis with a flame ionization detector at the University of Alberta (Kampbell and Wilson, 1989; Kampbell and Vandegrift, 1997). Samples were analyzed in triplicate and the results compared to a standard calibration curve. The calibration curve of Peak Area vs. CH_4 concentration was generated by injecting seven different known concentrations of CH_4 into the GC in triplicate (data included in Appendix F). To generate headspace in the sample vial, a 4ml sample of N_2 gas was then injected into each sampling vial and allowed to equilibrate with the liquid sample. A subsample of this gas was then withdrawn and injected into the GC to

determine the concentration of CH_4 in the headspace gas. The concentration in liquid was calculated by the relation as previously derived by Kampbell and Vandegrift (1997):

$$C = MW\left[\frac{55.5}{H} + \frac{V_g}{V_w}\frac{1}{22.4}\frac{273}{(T+273)}\right]X_g \qquad [16]$$

where: MW = molecular weight of the gas (16 grams/mole for CH_4)

H = Henry's Constant for Gas (41300 for CH_4 at 25°C)

V_g = Volume of headspace gas (4ml)

V_w = Volume of liquid (39.8ml, measured in triplicate)

T = Temperature (degrees Celsius)

X_g = Partial pressure of the gas (concentration detected by GC)

The data used to calculate the dissolved methane concentrations are included as Appendix F.

4.3.2 Field Hydrogeological Testing

During each of the three field visits, measurement of the hydraulic head in selected monitoring wells was carried out. Permeability testing of one monitoring well was attempted.

4.3.2.1 Groundwater Table Investigations

In order to determine the direction of groundwater flow and the gradient across the site, groundwater elevations were measured at nine HydroPunch® holes when they were pushed, and at six monitoring wells across the site on three occasions (15 June, 6-8 August, and 2-7 October 1998). A total station survey was performed to accurately determine the location and elevation of the wells and test holes.

4.3.2.2 Permeability Tests

Slug testing provides an efficient means of estimating the hydraulic conductivity of a formation around a borehole. A solid PVC slug 0.67m in length was used to displace water in the well. An automated datalogger attached to a pressure transducer in the well recorded data every second as the water level responded to either the addition or the removal of the slug. Tests were

repeated at least four times. The resulting data were interpreted using the Bouwer-Rice solution (Bouwer, 1989) with the aid of AQTESOLV™, a hydrogeological analytical software package.

Slug tests were attempted in monitoring well MW-01, however the fast response of the water table prevented meaningful interpretation of the results. Because the water table resided within the screened interval at the time of testing, displaced water was able to flow into the unsaturated zone, which offered less resistance to flow. Measurements were successfully achieved in three monitoring wells in a similar geologic unit 500m to the north (Biggar and Mullick, 1999). Slug tests in wells screened in the same geologic formation and confirmed with laboratory permeameter tests on soil samples were also carried out 1200m to the east (Thielmann, 1997).

4.4 Geological Analysis

The soil moisture content (w) and fraction organic carbon (f_{OC}) were characterized by laboratory analysis of samples gathered at the site. The geologic setting at the FFTA was interpreted by combining information from previous subsurface investigations with the borehole logs for MW-01 and AH-21 (Appendix A). Supporting information was obtained from the response of water flow into the HydroPunch® push rods.

4.4.1 Laboratory Characterization: Moisture Content and Fraction Organic Carbon

Analysis of moisture content (w) was carried out on three samples, one from 5.6m depth in MW-01 and two others gathered from the base of the excavated pit below the water table. Tests were carried out in triplicate following the method recommended by the ASTM D2216-80. Results indicated that the average moisture content of the aquifer is 15 ± 2%.

The fraction organic carbon (f_{OC}) is the mass ratio of organic carbon to soil and was determined for the two samples obtained from the base of the excavated pit following moisture content analysis. The method used is described by ASTM D2974-87. Tests were carried out in triplicate and the muffle furnace set to 440°C to burn off soil organic material. Results indicated

that the average fraction organic carbon in the aquifer is 0.3 ± 0.2%. The data collected for the calculation of the moisture content and fraction organic carbon are included as Appendix B.

4.4.2 Geologic Profile

The stratigraphy at the FFTA is made up of two silty sand horizons sandwiching a silty clay till layer of variable thickness (Figure 4). At the south end of the site, a 1.0-1.5m thick layer of medium to fine grained silty sand overlies a 2.5-3.0m thick silty clay till layer. Below the till is a medium to coarse grained, locally well sorted silty sand layer present to at least 11m depth in boreholes drilled off the southeast end of the excavation. The lower sand does not appear in boreholes drilled up to 11m depth off the northwest corner of the excavation, indicating that the till layer gradually thickens downwards to the north and northwest of the excavation. Two boreholes at the northeast corner of the site indicated that the contact between the till and lower sand is gradational and the grainsize increases with depth over a 1.0-2.0m thick silt horizon. Inspection of the pit walls in the southeast corner confirms the presence of three distinct and continuous horizons. The base of the till appears to thicken from approximately 3.5m below ground level at the southeast end of the excavation to over 10m depth both at the north end of the excavation and also to the northeast, at the location of HP-17, HP-18, and HP-19. A cross section of the geologic stratigraphy oriented in a north-south direction is included as Figure 4.

The till layer acts as an aquitard separating an unconfined perched aquifer in the upper sand from the lower sand aquifer. The perched water table in the upper sand appeared to be discontinuous across the site. The aquifer in the lower sand unit near the hydrocarbon source is unconfined, and less than half a metre below the base of the excavation. A discontinuous skim of free product was evident on the water table within the southeast portion of the excavated pit.

HydroPunch® holes 17, 18 and 19 had limited to no recovery when pushed less than 8.5m suggesting the lower sand layer is not present until beyond this depth. In addition, when the water-bearing layer was punched into and the drill rods pulled up 0.5m at 10.0m depth in HP-19, the force of the groundwater entering the pushrods drove the screen back up inside the rods.

This suggests that the groundwater in the lower sand is likely under confined conditions to the northeast of the excavation.

4.5 Hydrogeological Analysis

Field measurements of water table elevation were plotted to assess the direction and magnitude of the gradient across the site. Combined with an estimate of hydraulic conductivity and porosity, this information permits calculation of the groundwater velocity. An estimate of the rate of contaminant migration across the site can then be made by accounting for adsorption, biodegradation, and dispersion.

4.5.1 Estimate of Hydraulic Gradient

Regional groundwater flow in the area to the east of the main runway on the base is essentially north and east toward Marie Creek, approximately 600m to the northeast of the FFTA.

The groundwater regime at the FFTA is complex due to the presence of two aquifers. The shallow perched aquifer in the upper sand layer appears to contain a limited amount of water. Test holes in the upper sand are either dry (3-02 from Dames & Moore, 1994) or exhibit limited moisture in the sand horizon (2-04, Dames & Moore 1994 and MW-01, AH-21 and HP-20 this study). The shallow groundwater is unconfined and field measurements of HP-20 indicate aerobic conditions dominate downgradient of the FFTA.

The deeper aquifer resides in the lower sand unit and appears to change from unconfined conditions near the excavation to confined conditions to the northeast. The direction of groundwater flow in this layer was interpreted from hydraulic head measurements (Table 6) contoured for wells screened across the lower sand (Figure 5). Results indicate that flow is towards the east with a gradient of approximately 0.015m/m, rather than towards the northeast as may be expected from the regional flow pattern. The local easterly flow may be explained by the thickening clay till unit, which acts as an aquitard. This observed behaviour is similar to the southeasterly flow direction suggested by the geophysical results in Dames & Moore, 1994. The estimate of 0.015m/m can be considered conservative given the pattern of decreasing gradient with distance "downstream" (Figure 5).

4.5.2 Estimate of Hydraulic Conductivity

The Bouwer-Rice solution for hydraulic conductivity based on slug test results requires estimation of a number of parameters including: the effective well casing radius, the porosity of the sand pack around the well screen, the anisotropy ratio, and the saturated thickness of the aquifer. The average hydraulic conductivity calculated for the sand aquifer 500m to the north was approximately $8x10^{-5}$ m/s (Biggar and Mullick, 1999). As the hydraulic conductivity was not successfully measured directly at the site (discussed in Section 4.3.2.2), the use of the data measured in wells 500m away at the former base landfill site must be treated with some caution. These wells were screened over the unconfined aquifer in the same upper sand unit found at the FFTA, however the aquifer of interest at this site resides in the lower sand unit.

Results from over 40 slug tests in eight wells screened in the same geologic unit 1200m to the east, and confirmed with permeameter testing, indicate the hydraulic conductivity is approximately $2x10^{-4}$m/s (Thielmann; 1997).

An estimate of the hydraulic conductivity can also be made based on the geologic materials at the site. The silty sand material of this aquifer typically exhibits a conductivity ranging from 10^{-3} to 10^{-5}m/s (Freeze and Cherry, 1979). Given this information, the expected value for the site as a whole can be estimated at $1x10^{-4}$m/s.

4.5.3 Groundwater Velocity

Given the gradient (change in groundwater table elevation) across the site shown by the groundwater elevation contours, and the hydraulic conductivity estimate, the horizontal specific discharge may be calculated using Darcy's Law:

$$v = ki \qquad [17]$$

where: v = the horizontal specific discharge (length/time)

k = the hydraulic conductivity (length/time), and

i = the gradient (length/length)

Given the geologic variability at the site, the expected value of hydraulic conductivity ($1x10^{-4}$m/s) may vary by up to an order of magnitude. The estimate of the gradient (0.015 m/m)

can also be expected to vary somewhat across this site. At a minimum, the gradient is likely 0.008 and at a worst case scenario may reach 0.019 (Figure 5).

The seepage velocity can be calculated by dividing the specific discharge (v) by the porosity of the aquifer (n). The porosity was estimated by the following technique. Assuming the sample was completely saturated, the void ratio was calculated by the relationship:

$$e = G_S \cdot w \qquad [18]$$

where: G_S = specific gravity of the soil solids (unitless)

w = water content (unitless or %)

The porosity (n) is related to the void ratio by:

$$n = e/(1+e) \qquad [19]$$

The water content (w) was measured at 15 ± 2% and the specific gravity of soil is often estimated at 2.65. The void ratio calculated by Equation 18, using these estimates, is 0.40. The porosity, calculated by Equation 19, is estimated to be 29%. Maximum, minimum and expected specific discharge (calculated by Equation 17) and the related estimate of seepage velocities are summarized below.

	Hydraulic Conductivity (m/s)	Gradient (m/m)	Specific Discharge (m/yr)	Seepage Velocity (m/yr)
Maximum	0.001	0.019	599	2066
Minimum	0.0008	0.008	20	70
Expected	0.0001	0.015	47	163

4.5.4 Retarded Contaminant Migration

Retardation of dissolved contaminant migration relative to the groundwater velocity occurs when contaminant molecules are sorbed to particles in the aquifer matrix. The coefficient of retardation (R) can be estimated from the relationship:

$$R = 1+(\rho_b K_d)/n \qquad [20]$$

where: ρ_b = dry bulk density of the aquifer (Mass/Volume)

K_d = distribution coefficient (Volume/Mass)

n = porosity (Volume/Volume)

The distribution coefficient (K_d) can be estimated for a particular contaminant by the relationship:

$$K_d = K_{oc} f_{oc} \quad [21]$$

where: K_{oc} = proportionality constant for the contaminant of interest, normalized for total organic content (Volume/Mass)

f_{oc} = fraction organic carbon (%)

The fraction organic carbon was measured to be 0.3 ±0.2%. Numerous studies have characterized the proportionality constant K_{oc} for individual BTEX compounds (Table 2). By using K_{oc} = 39 L/kg, the lowest value shown in Table 2 for benzene (the most mobile of the BTEX constituents), and f_{oc} = 0.1%, a conservative estimate of the distribution coefficient is calculated to be 0.039 L/kg.

The dry bulk density of the aquifer sand can be calculated based on the soil void ratio and assuming that it is completely saturated (S_r = 100%). The dry bulk density of the aquifer can then be estimated by the equation:

$$\rho_b = \frac{M_S}{V_T} = \frac{G_S \cdot \rho_w}{1+e} \quad [22]$$

where: M_s = mass of the aquifer solids

V_T = total volume

ρ_w = density of water (1 kg/L)

The bulk density calculated by this equation is approximately 1.90 Kg/L. The coefficient of retardation can then be estimated by Equation 20 to be 1.25. A summary of the values used for this calculation are shown below:

K_{OC} (L/kg)	f_{OC} (unitless)	K_d (L/kg)	ρ_b (kg/L)	n (unitless)	R (unitless)
39	0.001	0.039	1.90	0.29	1.25

The retardation coefficient (R) can be used to calculate the velocity of the contaminant plume as follows:

$$v_c = v_x/R \quad [23]$$

where: v_c = retarded contaminant transport velocity (m/yr)

v_x = advective groundwater velocity (m/yr)

R = coefficient of retardation (dimensionless)

By applying the conservative estimate of R = 1.25 and neglecting dispersion and degradation, the estimated contaminant migration velocities are therefore:

	Retarded Contaminant Velocity (m/yr)
Maximum	1653
Minimum	56
Expected	130

4.6 Chemical Analysis

A number of chemical characteristics of the soils and groundwater were measured both in the field and in the laboratory. Field measurement of the following groundwater parameters were made with probes in a flow-through cell: DO, redox, conductivity, pH, and temperature. Samples for laboratory analysis were taken after these parameters stabilized during well purging. With the exception of dissolved methane gas analysis carried out at the University of Alberta, all chemical analysis were carried out at Enviro-Test Laboratories (ETL), Edmonton utilizing the standing offer agreement between 4 Wing Cold Lake and ETL.

4.6.1 Field Groundwater Chemistry

Table 7 contains a summary of the groundwater parameters measured in the field with probes in a flow-through cell. Measurements can be compared to unpublished groundwater data from six selected shallow monitoring wells in central and northern Alberta summarized in Appendix C. These wells are monitored by the Environmental Division, Alberta Environment, and may be considered representative of the range of values for water quality parameters in uncontaminated shallow monitoring wells.

Measured values of pH ranged from 6.9 to 8.0, indicating that conditions are neutral and therefore at an optimum level for microbial growth. These values fall within the range measured at other shallow monitoring wells in Alberta.

Electrical conductivities measured during well purging were relatively low in the shallow perched aquifer (125μS/cm at HP-20). The deeper aquifer exhibited a wide range of conductivities from 300-1000μS/cm. A contoured plot of the data was generated (Figure 6) using a contouring software package (Surfer™, Scientific Software Group). The trend corresponds with a NW-SE trending conductive anomaly reported following geophysical testing in 1992 (Dames & Moore, 1994). This trend may represent an ionic solute plume and thus might indicate the groundwater flow direction within the deeper aquifer. The dominant fire fighting agent used to put out fires at the FFTA was an aqueous film forming foam (AFFF) which contains up to 10% salts in the concentrate by weight (MSDS sheet included as Appendix D). Salts of potassium are also present in the foam from hand-held extinguishers used to put out smaller fires in the burn pans at the site. Caution should be exercised in interpreting groundwater flow from these data however, as the high density of these salt-rich compounds may cause them to sink to the base of the sand aquifer. The resulting conductive anomaly could represent a trough in the bottom of the aquifer containing concentrated AFFF and not indicate flow direction.

Redox potentials were measured in groundwater samples to evaluate the redox conditions in the aquifer. Redox potentials varied only slightly in the lower aquifer from –35mV to –41mV. These values reveal conditions in the subsurface environment typical of iron reduction (Figure 1). Redox values for the selected comparable data set in central Alberta varied over a greater range than those measured at this site.

Temperatures monitored with the probes in the flow-through cell did not provide adequate accuracy because the water was slightly warmed during sampling. A more precise measurement of the groundwater temperatures was conducted in October 1998 with the use of a temperature transducer lowered into selected monitoring wells. These results, combined with probe measurements on HydroPunch® samples from the same time period indicate that groundwater temperatures averaged 9°C in the lower aquifer and 12°C in the shallow aquifer (measured at HP-20 only). This is approximately 3°C warmer than average values for groundwater temperature measured in shallow monitoring wells across central Alberta.

DO measurements will be discussed in the context of TEA analysis in Section 5.3. Results indicate that the DO levels lie within the typical range for a contaminated site and compare well with values from other shallow wells in central Alberta.

4.6.2 Contaminant Assessment Results

The contaminants of primary concern analyzed in soil and water for this study were BTEX. These compounds are the most soluble of all fuel constituents (Table 3) and are known to have both chronic and acute health effects in humans and aquatic organisms (ASTM, 1995). In addition, laboratory analysis included volatile (C5 - C10) and extractable (C11 - C30) hydrocarbons. Table 1 gives typical values for the relative concentration of compounds in JP-4, a jet fuel commonly used to ignite training fires at the site. Table 3 lists dissolved concentrations of the main water-soluble components of JP-4 fuel. These values provide an indication of the concentration of groundwater contamination that could be expected at the site. Analyses were performed on the groundwater at all sampling points from this study, a few previously installed monitoring wells, and on the soil from auger hole MW-01. A summary of the results of the chemical analysis from the June, August, and October sampling periods are contained in Table 8. Figure 7 contains a contoured map of dissolved BTEX concentrations measured in the groundwater.

4.6.2.1 Soil Vapour Contamination

Soil vapour results are included in the drill log for auger hole MW-01 (Appendix A). In soil sampled from MW-01, LEL levels were measured as non-detectable in five samples taken in the upper sand and till above the water table. One sample taken 2.5m below the water table (in the lower sand) at 7m depth indicated a 6% LEL. This provides supporting evidence of light non-aqueous phase liquid (LNAPL) hydrocarbon contamination in the lower aquifer near the excavation. It also correlates well with elevated levels of BTEX measured at the same depth in the soil and groundwater.

4.6.2.2 Soil Contamination

The reported detection limits for each of the BTEX compounds in soil (performed according to USEPA method 8020) were 0.01 mg/kg [ppm] (or 10μg/kg [ppb]). CCME recommended soil quality criteria for commercial/industrial land use for the BTEX compounds are 5, 0.8, 20, and 17 mg/kg (ppm), respectively (CCME, 1997). For residential/parkland land use the values are 0.5, 0.8, 1.2 and 1, respectively. Soil analyzed for hydrocarbon contamination (MW-01 and AH-21) yielded non-detectable levels of BTEX, and one sample contained trace amounts of both total extractable hydrocarbons (TEH) and total volatile hydrocarbons (TVH). These samples were located in the lower sand approximately 1m below the water table.

Summary of Soil Analysis for Hydrocarbon Contamination

Test Hole	Date	Method	Depth m	Benzene mg/L	Toluene mg/L	Ethylbenzene mg/L	Xylenes mg/L	TEH mg/L	TVH mg/L
MW-01	Aug	Split-spoon	5.5	<0.01	<0.01	<0.01	<0.01	17	3.6
AH-21	Oct	Solid Stem	4.5	<0.01	<0.01	<0.01	<0.01		

4.6.2.3 Groundwater Contamination

The detection limits for BTEX in water (performed according to US EPA method 8020) are approximately 10 times less than those in soil, at 0.001 mg/L [ppm] (or 1μg/L [ppb]). CCME interim quality criteria for drinking water (CCME, 1995) for the BTEX compounds are 5, <24, <2.4, and <300 μg/L (ppb), respectively. For freshwater aquatic life the values are 300, 300, 700, and undefined μg/L (ppb), respectively. There are no values listed for livestock watering or irrigation for these compounds. These values are not well suited for remediation criteria for this industrial/ commercial site, as the groundwater is not used for any of the stated applications. However, they do provide an indication of the magnitude of possible acceptable concentrations for the compounds. A complete listing of analytical results for the groundwater samples is contained in Table 8.

Maximum measured values of dissolved phase BTEX were 1400, 37, 460, 2700 ug/L respectively, in MW-L immediately adjacent to the east wall of the existing excavation. At 40m to the southeast (HP-02), dissolved phase BTEX concentrations had dropped to approximately one quarter of the peak values (380, 1.6, 170, 540 ug/L respectively). By 80 meters to the east, BTEX

concentrations were at or below the limits of detection (HP-17 & HP-03). The peak contaminant levels are approximately 17% of the highest concentration of total BTEX that can be expected in groundwater in contact with JP-4 fuel (Wiedemeier et al., 1995), suggesting that only a small amount of free product likely remains in the aquifer.

Duplicate analyses were carried out on groundwater sampled from HP-16 as a check on laboratory quality assurance, and both analyses showed non-detectable BTEX concentrations. Rinsate blanks and duplicates were also analyzed at the Old Imperial site (Table 12) and during a concurrent investigation at the former base landfill (Biggar and Mullick, 1999). The results also validated the sampling technique and the laboratory analysis.

Considering the direction of groundwater flow and the location of the peak contaminant levels at the site (Figure 7), it is possible that dissolved phase BTEX may have migrated to the southeast, further south than the eastern line of sampling locations was extended. The detailed survey of the location of the wells and HydroPunches was not performed until November, 1998. Analysis of the groundwater flow direction was performed subsequently. As a result, the apparent direction of groundwater flow in the lower aquifer to the east came as a surprise. Generally in this area groundwater flow is to the northeast towards Marie Creek. The previous investigations at the site had not adequately defined the local groundwater flow direction. The result was that sampling was skewed to the northeast, and inadequate sampling was carried out in the true direction of groundwater flow. To confirm the actual extent of groundwater transport of BTEX at the site some additional sampling will have to be carried out, details of which are contained in Section 4.9.1 of this report.

4.6.3 Electron Acceptor Analysis

To assess the microbial activity and the associated geochemical changes in groundwater, analysis of the depletion of TEAs (used by the microbes when they degrade organic compounds) was performed. The TEAs analyzed in this study were dissolved oxygen (DO), nitrate (NO_3^-), which is first reduced to nitrite (NO_2^-) and ultimately to nitrogen gas (N_2), and sulfate (SO_4^{2-}). In addition, generation of the by-products of microbial degradation of organic

compounds was considered. The degradation by-products analyzed in this investigation include iron (II) (Fe^{2+}), sulfide (S^{2}), and methane.

Figure 8 presents selected geochemical data gathered from water samples in a traverse roughly parallel to the direction of groundwater flow in the lower aquifer. Depleted DO levels were measured both in the source area and immediately downgradient. Neither nitrate nor nitrite was measured at significant levels either upstream or within the plume, suggesting that nitrate reduction is not a significant TEAP at this site. The average concentration of dissolved iron downstream of the source increased from 50 to 150 mg/L indicating that iron reduction may have been occurring, but a high background concentration (measured in duplicate on separate occasions in HP-4 and HP-16) at the site prevents an unequivocal conclusion. The average background concentration of sulfate decreased from 12 mg/L upstream to 4.6 mg/L downstream of the source. Trace levels of sulfide were detectable downstream of the source area indicating that sulfate reduction was likely occurring. Dissolved methane gas increased from non-detectable background levels to 7 mg/L immediately downgradient from the source and decreased again to non-detectable levels further downstream. This evidence indicates methanogenic activity within the plume.

4.6.4 Contaminant Mass Balance through Stoichiometry

An estimate of the contribution of each redox process to the total contaminant mass biodegraded can be achieved by applying the stoichiometry of the chemical reactions describing the oxidation of BTEX (Equations 1-5, Section 2.1). Based on these relationships, the mass ratio of TEA required to oxidize an equivalent amount of hydrocarbon can be calculated. Metabolic by-product concentrations (Fe^{2+}, CH_4) can be correlated to the mass of hydrocarbon degraded in the same fashion. A summary of the mass ratios for TEAs or metabolic by-products to total BTEX degraded is included as Table 9 (the ratio is averaged for each BTEX constituent). By assuming that the change in each electron acceptor/metabolic by-product concentration across the contaminated site is due solely to the biodegradation of BTEX, the relative contribution of each redox process can be assessed. This calculation also assumes that each reaction runs to completion (and degrades BTEX molecules only, not intermediates partially degraded by another

process) and that no substrate is taken up as biomass. The results of this analysis are also summarized in Table 9 and indicate that the anaerobic processes are by far the most significant. Because methanogens only degrade the by-products of other degradation reactions (typically H_2, CO_2, and acetate), the amount of BTEX degraded by this stoichiometric relationship (Equation 5) should not be considered a separate mechanism that uniquely contributes to the total amount of BTEX degraded. The amount of BTEX degraded by this stoichiometric relationship most likely represents the total capacity for both aerobic and anaerobic BTEX degradation at the site. If it is assumed that the total BTEX biodegradation capacity can be calculated based on the concentration of dissolved methane alone, then the ability to degrade approximately 9.5mg/L BTEX per litre groundwater exists at the site. If it is assumed that aerobic respiration, iron (III) reduction, and sulfate reduction can be added together to account for a combined BTEX degradation capacity, then the geochemical data suggest that the site has the ability to degrade approximately 2.7mg/L BTEX per litre groundwater by these TEAP. The large difference in these calculated capacities and the relatively large concentration of dissolved methane in the groundwater suggests that the methanogenic degradation process is an important TEAP at this site. The total calculated BTEX biodegradation capacity of approximately 9.5mg/L exceeds the measured maximum BTEX concentration (4.6mg/L), suggesting that an adequate biodegradation capacity exists at the site.

4.7 Microbial Analysis

Another line of evidence for intrinsic bioremediation is provided by an investigation of the *in situ* microbial community. A laboratory test was performed to enumerate microbes from a soil sample at the site by classifying them into broad categories based on the method they use to obtain their carbon and energy for metabolism. Direct measurement of microbial activity by laboratory batch-type experiments was also performed to analyze the rate and extent of microbial activity under different environmental conditions.

Samples for microbial analysis were taken from two sites, both at or just below the water table within the lower sand layer near the excavation: MW-01 at 5.5m depth for microbial enumeration, and AH-21 at 4.7-5.4m for biodegradation rate analysis.

4.7.1 Microbial Enumeration

The most probable number (MPN) technique was employed for soil microbe enumeration. This approach is widely used in microbiology and provides a straightforward and simple means of making an order of magnitude scale estimate of the quantity and type of microorganisms present at the site.

4.7.1.1 Enumeration Methodology

The MPN method utilizes statistical analysis of bacterial growth in replicate test tubes containing a serially diluted sample (Alef and Nannipieri, 1995). A soil sample was gathered in the same manner as for chemical analysis within the contaminant plume at 5.6m depth (MW-01). Tenfold serial dilutions up to 10^{-7} were prepared and inoculated into liquid media appropriate for measuring nitrate/nitrite reducers, iron reducers, sulfate reducers, JP-4 degraders, and total heterotrophs. Each medium was designed to enumerate specific classes of microbes: for example, in this study a mineral salts medium supplemented with filter-sterilized JP-4 jet fuel was used to specifically enumerate microbes capable of utilizing JP-4 hydrocarbons. Nitrate-, iron(III)- and sulfate-containing media were used to selectively determine the nitrate-, iron-, and sulfate-reducing components of the total microbial population. A complete description of the five liquid media recipes is included as Appendix G.

Each dilution bottle (10^{0} through 10^{-7}) was dosed with 90ml of 0.1% (by volume) sodium pyrophosphate. Ten millilitres of medium was dispensed into each test tube (approximately 40 tubes per medium). For the analysis of nitrate-reducing bacteria (NRB), an inverted Durham vial was added to each test tube in order to assess the production of gas. For the test tubes used to analyze sulfate reducing bacteria (SRB), two ¾" bright finishing nails were added. The dilution bottles, rubber stoppers, pipettes, test tubes and caps were then sterilized in an autoclave and cooled to ambient temperature. Ten grams of sample soil was then added to a dilution bottle,

recording the weight to ± 0.1grams. After 30 minutes of agitation on a reciprocating shaker, 10ml of soil and groundwater sample was transferred to a fresh dilution bottle using a sterile widemouth pipette. This bottle was then inverted and mixed thoroughly, and 10ml of sample withdrawn with another sterile widemouth pipette. This was transferred to another dilution bottle and the serial dilution process was iterated until all 7 dilutions were completed. Five replicate test tubes of medium were aseptically inoculated with 1ml of each dilution and covered with sterile caps. This was repeated for each of the five media. One or two uninoculated test tubes for each medium were included as negative experimental controls. Positive controls were prepared by inoculating each medium type with 1ml of an appropriate bacterial culture known to represent the bacterial group being enumerated (Appendix G). The test tubes were incubated at 6°C for 4 weeks and then a further 2 weeks at 22°C, and were scored weekly for positive results.

An additional test was carried out on selected test tubes containing the NRB media to assess the presence of nitrite (Daniels et al., 1994). After 4 weeks of incubation, subsamples of the inoculated media were mixed with 1ml each of solutions containing 0.8% sulfanilic acid reagent and 0.5% N,N-dimethyl-alpha-naphthylamine. The appearance of a pink or red colour indicated the presence of nitrite. The addition of up to 5mg of zinc powder (Fisher Scientific) to colourless solutions would chemically reduce nitrate to nitrite (inducing the colour change) and confirm that the nitrate had not been completely reduced to N_2.

4.7.1.2 Enumeration Results

Positive indicators of growth for each media type are as follows. The presence of viable heterotrophic bacteria was indicated by appearance of turbidity or flocs greater than that observed in uninoculated negative controls. For hydrocarbon degraders, the presence of turbidity or flocs associated with the pool of JP-4 at surface was considered a positive indicator. For the sulfate reducers, the presence of a black precipitate (iron sulfides) on the nails was considered a positive result. The presence of iron reducing bacteria was indicated by a significant colour change at the base of the semi-solid medium in the test tubes. Nitrate reduction to nitrite was

indicated by a colour change in subsamples analyzed as described above. Complete reduction to nitrogen gas was indicated by the presence of gas bubbles in the inverted Durham vials.

Once the number of positive tubes was tabulated, the MPN was calculated based on the characteristic number and the dilution level of the positive tubes (Alef and Nannipieri, 1995). The characteristic number is a three-value sequence describing the number of positive tubes in three adjacent rows, starting with the least concentrated dilution in which all tubes have been recorded as positive and moving towards increasing dilution. The most probable number of bacteria can then be read from a statistical table (Alef and Nannipieri, 1995). Subtle corrections were then applied to the results to account for the actual mass of soil used in each sample, and for the soil moisture content. Results are expressed as MPN/gram dry soil. The 95% confidence interval for the data also comes from the statistical tables (Alef and Nannipieri, 1995). The confidence limits only reflect the influence of statistical variations on results and not all sources of variation. The MPN was calculated after incubation for 4 weeks at 6°C and again after 2 additional weeks at 22°C.

MPN results after 4 and 6 weeks did not differ significantly. While this may indicate that the microorganisms were acclimated to cold temperatures, it is not possible to conclude this with any certainty. The populations of NRB and Total Heterotrophs were approaching the upper limit of detection at 4 weeks, and the differentiation between positive and negative tubes for the hydrocarbon degraders was initially too subtle to detect. An additional 50μL of sterile JP-4 was added to each test tube at week 4 to attempt to make positive tubes more obvious. As a result, the only enumeration results discussed in this thesis report will be the MPNs calculated at week 6. Details of the data used to calculate the MPN results are included in Appendix G.

As indicated in Figure 9, significant populations of microorganisms were detected in the order of 10^7 total heterotrophs/gram dry soil. Hydrocarbon degraders were also detected at significant population levels (>10^5/g) at the site. The dominant family of microorganisms present appeared to be nitrate and nitrite reducers, which were measured at 10^7/g. However, the lack of nitrate and nitrite concentrations in the groundwater suggests that the site may be nitrate limited. Many denitrifying bacteria are facultative (able to survive in an aerobic or an anoxic environment)

and may be surviving through utilization of an alternate TEA *in situ*. Microorganisms capable of iron reduction were detected at marginally significant levels (10^2/g) and geochemical data were inconclusive regarding iron reduction. SRB were not detected in significant numbers despite geochemical evidence suggesting that sulfate reduction was occurring. Similar results were recorded in a sample handled completely anaerobically (Section 4.7.2.3), and a similar failure to detect SRB occurred during a study at the nearby main fuel storage compound in 1997 (Biggar, 1998b). It is possible that SRB occur in very low numbers at this site and that sulfate was being reduced in the groundwater by another process or that the SRB were not successfully cultured.

4.7.2 Microbial Activity

A radiorespirometric laboratory investigation was carried out on soil sampled from within the plume to study the rate and extent of toluene mineralization. The purpose of the investigation was to confirm the potential for biodegradation and assess rates under the cold temperature conditions at the site. A known amount of radiolabelled toluene was added to serum vials containing a slurry of soil and groundwater from the contaminated zone. The appearance of the radiolabelled carbon as carbon dioxide ($^{14}CO_2$) in the vials provided direct evidence for the microbial biodegradation of the radiolabelled toluene. Measuring the $^{14}CO_2$ concentration increase with time indicated the rate of biodegradation, and rate constants were calculated.

4.7.2.1 Methodology for Microbial Activity Experiment

Three experimental settings were tested to analyze the potential for biodegradation and to investigate the effects of temperature on the rate and extent of mineralization:

- Aerobic, 8°C
- Aerobic, 22°C
- Anaerobic, 8°C

The contaminated soil was mixed at a ratio of 1kg soil to 0.5L sterile double-distilled deionized water and 0.5L groundwater. The groundwater was obtained from MW-L and MW-K to provide nutrients and TEAs that reflect *in situ* conditions. Fifty millilitre aliquots of the slurry were aseptically transferred with a wide mouth pipette into 158mL glass serum vials. Each vial was

then dosed with 50μL filter-sterilized JP-4 containing 79,000 disintegrations per minute (DPM) [methyl-^{14}C] toluene (Sigma Chemical Co.) using a 25μL Lambda glass pipette. Each vial was then capped and crimped with a Teflon®-lined butyl rubber stopper (Fisher Scientific). The anaerobic trial was prepared similarly to the aerobic trials in 125mL serum vials except that each headspace was replaced with a mixture of 10%CO_2/ 90%N_2 gas during inoculation and capping. Sterilized negative controls were prepared as above, but autoclaved twice for 60 minute periods on consecutive days. Positive controls were prepared by inoculating randomly selected vials with 1mL of a known JP-4 degrading mixed bacterial culture through the vial septum. Nutrient-amended control samples were similarly dosed with 0.1mL of a sterile 50X N, P solution (recipe in Appendix G). Samples were incubated at the appropriate temperatures, in the dark, under static conditions. The incubator was monitored with a datalogger equipped with a thermister to ensure that incubation temperatures did not vary significantly. For each test condition, more than 60 sample vials were prepared with four vials sacrificed at each time interval (one sterilized control, and three test vials).

Measurement of $^{14}CO_2$ entailed acidifying each vial with 1mL 4N H_2SO_4 to convert bicarbonate to carbon dioxide and then flushing the headspace of the vial for 15 minutes through a CO_2 trapping apparatus (Figure 10) with N_2 gas at approximately 100ml/min (Fedorak et al., 1982; Brown et al., 1991). The amount of acid required to lower the pH of the slurry below 2 was confirmed by testing with pH paper. The acidified sample vials were set in crushed ice prior to and during flushing to minimize the volatilization and transport of unconverted radiolabelled toluene. The first liquid scintillation vial in series contained 10ml of ACS fluor (Amersham), which captured any unconverted radiolabelled toluene carried by the nitrogen gas. The $^{14}CO_2$ trapping fluid added to the second and third liquid scintillation vial in series was 10ml of ACS fluor and 1mL of Carbazorb® (Packard), a CO_2 trapping fluid. The flushing time required and the volume of Carbazorb® required were determined using test samples dosed with $H^{14}CO_3^-$ prior to flushing the true experimental trials. Tests were performed in triplicate and the radioactivity levels in the scintillation vials were measured in a liquid scintillation counter (Beckman LS 3801). The flushing

apparatus was periodically checked for leaks by flushing and measuring a known amount of $^{14}CO_2$ through the system.

4.7.2.2 Trends in Biodegradation Rate Study Data

The results of the measurements of radioactivity levels were expressed as a percentage: net $^{14}C_{RECOVERED}$ as $^{14}CO_2/^{14}C_{DOSED}$. The amount of radioactivity in the ^{14}C toluene initially added to each vial was 79000 DPM (average of duplicate measurement prior to addition to vials). The net $^{14}CO_2$ recovered was calculated by subtracting the total $^{14}CO_2$ (vials 2 +3, Figure 10) measured in sterile controls from the total $^{14}CO_2$ measured in the experimental trials. Background levels of radioactivity were measured each time serum vials were flushed by measuring the radioactivity detected in a scintillation vial containing only ACS Fluor. Consistently low levels were detected throughout the experiment. Records of the experimental data are included as Appendix H. The calculated net $^{14}CO_2/^{14}C_{DOSED}$ values were plotted against the corresponding time at which they were flushed for evaluation.

Several interesting trends are apparent in the radiorespirometric study results (Figure 11). The aerobic samples exhibited a brief lag period of limited $^{14}CO_2$ production, followed by a period of rapid $^{14}CO_2$ evolution. This latter phase can be interpreted as the maximum possible toluene biodegradation rate for each condition. Following the rapid mineralization stage, $^{14}CO_2$ production slowed dramatically as conditions likely became limited by the availability of substrate, nutrients, or TEAs. As expected, the aerobic sample incubated at 22°C exhibited the quickest conversion to $^{14}CO_2$ reaching a maximum conversion ratio between 50-60%. The rest of the ^{14}C toluene may have been converted to microbial biomass with smaller amounts persisting as intermediate degradation products and unconverted toluene. The sample incubated at 8°C exhibited slower mineralization rates, and conversion to $^{14}CO_2$ reached approximately 40-50% at the maximum extent. As anticipated, the anaerobic sample incubated at 8°C exhibited both the lowest conversion rate and the lowest extent of $^{14}CO_2$ production over the study period.

Overall, the nutrient-amended controls did not exhibit $^{14}CO_2$ concentrations significantly different than the non-amended samples (Figure 12). The nutrient-amended FFTA samples at

8°C (Figure12a) suggest a marginally higher conversion rate, but the lack of difference at 22°C and in the anaerobic samples suggests this may not be significant or truly representative. The similarity between the non-amended and the nutrient-amended samples suggests that the microbial degradation of contaminants at these sites is not likely nutrient limited. Positive experimental control cultures containing known toluene degrading microorganisms also exhibited similar mineralization patterns to the site trials (Figure 12), which confirms the experimental methodology.

Another means of checking the validity of the experimental data was to plot the levels of apparent $^{14}CO_2$ (more likely this was unconverted ^{14}C toluene) that were detected in vials 2 and 3 of the sterile controls against time. The consistent low levels of apparent $^{14}CO_2$ measured in the sterile controls indicate that no biodegradation occurred in these samples (Figure 13). The high values observed at Day 125 may be due to radioactive contamination in the flushing apparatus, and the data from this one day does not alter the experimental interpretation.

Since these trials were carried out under conditions similar to those existing in the field, the results provide strong evidence for both aerobic and anaerobic capacity for biological degradation of contaminants of concern under *in situ* temperatures and geochemical conditions. Further discussion of these experimental results is included as Section 6.

4.7.2.3 *Additional MPN Analysis of Microbial Community in Batch Vial*

To investigate the microbial community present in the anaerobic radiolabelled sample vials, an additional MPN analysis was carried out on one soil sample at Day 126 of incubation. The soil sample was prepared by flushing the vial with N_2 through a sterile flushing apparatus to remove radioactivity. The sample was not acidified in order to protect the microorganisms. The enumeration method followed was similar to that described in Section 4.7.1.1, except that the serial dilutions and incubation were carried out in an anaerobic glove box. The atmosphere in the glove box was approximately 85% N_2, 10%H_2, and 5%CO_2. Based on the previous results, only 4 serial dilutions for SRB and 9 serial dilutions for NRB were prepared. The additional test for

nitrite was not carried out, so positive evidence for nitrate reduction came only from the complete reduction of nitrate to nitrogen gas, captured in the inverted Durham vials in the test tubes.

The data used in the calculation of the MPN for each medium type are included in Appendix G. The results are displayed graphically in Figure 14 and indicate that nitrate reducing bacteria are the most significant anaerobic group enumerated. These results further validate the aerobic MPN analysis, and indicate that the high number of positive tests in that enumeration weren't due to contamination with facultative aerobic microbes. Overall, the results are quite similar to those of the previous enumeration. Total Heterotrophs were measured in the order of 10^6/gram dry soil. JP-4 degraders were present in significant numbers (10^3/g) and a marginally significant population of iron reducing bacteria was detected (10^2/g). Once again, sulfate reducing bacteria were not detected in significant numbers in this exercise implying that the failure to detect SRB in previous enumerations (Section 4.7.1.2) was not likely due to mishandling or exposure to air. These results suggest that, based on the high population of nitrate reducers present in the soil, nitrate reduction may have been a dominant TEAP at the FFTA. The lack of nitrate in the groundwater across the site does not support this conclusion, however.

4.7.2.4 Simple First Order Rate Interpretation

First order kinetics are often used to model biological processes, including the biodegradation of organic contamination in groundwater (MacIntyre et al., 1993; Chapelle et al., 1996). Simple first order kinetics can be expressed mathematically as:

$$C_t = C_o e^{-kt} \qquad [24]$$

where C_t = the concentration at time "t"

C_o = the initial concentration

e = base of the natural log = 2.7183

k = the first order rate constant

t = time

Rearranging the equation gives:

$$\ln (C_t/C_o) = -kt \qquad [25]$$

Plotting ln (C_t/C_o) versus time will yield a line whose steepest slope is the maximum rate constant, k (Figures 15-17). Assuming that 32% of the ^{14}C radiolabelled toluene remains unconverted (the greatest recovery as $^{14}CO_2$ was 68%), the amount of toluene remaining at any time, t, may be calculated as (100% - [100/68 x $^{14}CO_{2\ measured}$%]. This assumption is a somewhat artificial construct and limits the rate constant estimate to an order of magnitude approximation. This analysis was performed on all the experimental results, a summary of which is provided in the table below. Comparing rate constant results to typical values requires determination of the half-life ($t_{1/2}$); the time at which $C_t/C_o = 0.5$. Thus:

$$t_{1/2} = \ln(0.5)/(-k) = 0.693/k \qquad [26]$$

The experimentally determined half-life that was calculated for toluene under aerobic conditions at 8°C is approximately 0.05 years. This value ($t_{1/2}$=0.05) is at the lower end of the reported range (ASTM, 1995) indicating reasonably rapid degradation and implying that these microbes are well acclimated to their environment. This conclusion should be treated with caution, however, as it has been suggested that biodegradation rates determined for samples under aerobic or denitrifying conditions in laboratory studies may not reflect the rate observed in the field (Wiedemeier et al., 1995). The aerobic biodegradation half-life for toluene at 22°C was even shorter (0.03 yr), and the half-life for anaerobic degradation at 8°C was approximately two orders of magnitude longer (1 yr).

First Order Toluene Biodegradation Rate Constant

Conditions	Maximum Rate Constant, k (day^{-1})	Maximum Rate Constant, k (yr^{-1})	Maximum Rate Half Life, $t_{1/2}$ (yr)
Anaerobic 8°C	0.002	0.7	1
Aerobic 8°C	0.04	14	0.05
Aerobic 22°C	0.07	24	0.03
Typical Aerobic Range*	-	4 – 35	0.02-0.17

*ASTM, 1995

4.7.2.5 Alternative Model for Microbial Activity: Declining Growth Model

The mathematical equations most commonly used to model intrinsic biodegradation apply first order kinetics (Odermatt, 1997). The application of rudimentary first order kinetics has the advantage of simplicity, but the assumptions required may be unrealistic with the result that

the estimated rate constants may not adequately characterize the reaction rate. The Declining Growth model is a more complex mathematical relationship that can better describe the experimental data pattern (Odermatt, 1997; Ellert and Bettany, 1988). This is particularly useful for the comparison of rate constants under differing temperatures. While it is not appropriate to compare reaction constants for the different temperatures between models, the quantitative comparison of constants derived by the same model at different temperatures can be useful. Models provide only indirect evidence of the mechanisms responsible for the observed pattern of mineralization. More precise measurements of microbial growth, the microbial community structure, and enzyme activities will be required to explain these results in microbial and chemical terms (Ellert and Bettany, 1988).

Another model that has been applied to biological growth, including the aerobic and nitrogenic degradation of wastewater (Tchobanoglous and Burton, 1991), is the declining growth model. The mathematical formulation of this modified first order model describes a curve whose positive slope gradually decreases as it approaches a maximum horizontal asymptote. The biological basis for this decreasing growth trend relates to the study of population dynamics under substrate limited conditions (Odermatt, 1997).

The form of the equation is:

$$C_t = C_{max}(1-e^{-kt}) \qquad [27]$$

where: C_{max} = the concentration of potentially mineralizable toluene (mass/volume)

This model can account for the decreasing rate of growth with time evident in the experimental data set (Figure 11), but not for the initial lag period. It has been shown that microorganisms take up approximately 50% of organic substrate as biomass during the log growth phase (Tchobanoglous and Burton, 1991). In order to account for substrate taken up by the microbes as biomass, it was assumed that the amount of ^{14}C-toluene that was actually degraded was twice the amount detected as $^{14}CO_2$. Therefore, the model was fit to $2x^{14}CO_2$ (detected) in order that the parameter C_{max} reflect the expected maximum degradation in the sample vial. The models were applied to the transformed experimental data and the parameters C_{max} and k were derived by the method of least squares (the residual sum of squared error

between the model prediction and the laboratory measurement was minimized). In order to account for the lag, the model was forced through trial lag periods and the model outcomes compared via the sum of the squared residuals and the Pearson's Moment (R^2 = 1-(Sum Squares Residual/Sum Squares Total)). The model fit to the experimental data is shown in Figures 18-19. The validity of the model was also tested by a residual plot (experimental - predicted value vs. time) for each data set. The random scatter of residuals over a narrow range of error supported the validity of the model (Appendix I). A summary of the parameter estimates is provided below:

The parameter estimates are similar to those derived from the simple first order modeling, but the application of this model allows a quantitative comparison of the extent of mineralization. Based on the estimates of C_{max}, the extent of toluene conversion to $^{14}CO_2$ is approximately 20% greater at 22°C (107%) than it is at 8°C (83%). The biodegradation half-life calculated for the aerobic sample at 8°C (0.023 yr) is approximately double that at 22°C (0.013yr). Inspection of the data for the anaerobic setting suggests that the relatively large margin of error on the experimental data casts significant doubt on the relevance of the parameter estimates using this model. As a result, the statistically determined estimates of anaerobic reaction rate and maximum extent of reaction are unrealistic and indefensible with this model. A summary of the parameter estimates is included below:

Declining Growth Rate Model Parameters

Sample	Lag Period (days)	C_{max} (% $^{14}CO_2/^{14}C_T$)	k (yr^{-1})	$t_{1/2}$ (yr)	R^2
FFTA Aerobic 8°C	7	83	29.65	0.023	0.99
FFTA Aerobic 22°C	5	107	54.78	0.013	0.98

4.8 Groundwater Modeling

To gain a better understanding of the significance of biodegradation and to make predictions about future plume migration behaviour, a numerical computer model was applied to the site. Given the variable character and limited extent of field measurements of contamination at the site, a comparatively simple two-dimensional model was selected as the most appropriate design.

The intent of this modeling exercise was twofold. By calibrating a numerical model to the current conditions, an estimate of the magnitude of the biodegradation component of the contaminant mass balance could be achieved. Because the contaminant source has been removed with the cessation of fire fighting training activities, the calibrated model could then used to predict future plume configurations by performing additional simulations without the contaminant source term.

The overall contaminant modeling process began with a conceptual model of the site, generated by field, laboratory and historical data. A mathematical computer code was then selected to describe the groundwater flow and contaminant transport at the site. The model was implemented by selecting input parameters and boundary conditions that best reflected the conceptual model. The groundwater flow model was calibrated to field measurements of hydraulic head by adjusting the transmissivity values across the aquifer. The contaminant transport component of the model was then calibrated to field measurements of BTEX concentration in the groundwater. The resulting model was tested for its sensitivity to variations in input parameters. Once confidence was gained in the robustness of the model, it was used to predict the environmental fate of the contaminant plume concentrations.

4.8.1 Site Conceptual Model

Synthesizing the data gathered from the field into a conceptual model provides a starting point for the computer modeling exercise. The following describes the conceptual model based on this synthesis.

The contaminant source was an intermittent dose of hydrocarbon applied to the soil surface on a weekly basis for forty years from when the area was first used for fire fighting training in the 1950's. The hydrocarbon, dominantly jet fuel, migrated downwards through the upper sand, and through fissures or discontinuities in the till layer until it reached the water table in the lower sand unit. A pool of LNAPL may or may not have formed on the water table, and a plume of dissolved phase hydrocarbon migrated to the east in the direction of groundwater flow due to the forces of advection and dispersion. The plume migration was mitigated by the adsorption of contaminant onto soil particles within the aquifer matrix, and by the oxidation of

contaminants due to biodegradation. The high rate of biodegradation, both anaerobic and aerobic, caused plume migration to reach a steady state condition less than 25 years after contamination was introduced into the environment. Groundwater flow in the system is considered steady state and is locally influenced by the variable thickness of the aquifer and changes in hydraulic conductivity such that most of the hydraulic head loss (and therefore highest velocity) occurs through the source area. The head loss (and therefore velocity) is reduced downgradient of the source either by an increasing aquifer thickness or a decreasing hydraulic conductivity.

4.8.2 BIOPLUME II Code Overview

A review of available software suggested that BIOPLUME II Version 1.1 was a two-dimensional solute transport model that could perform the required analysis given our limited data set (Rifai et al., 1987). BIOPLUME II was designed to simulate the transport of dissolved hydrocarbons in groundwater under the influence of aerobic biodegradation. In addition, it has the ability to simulate reaeration and anaerobic biodegradation using specified first order decay constants. The model is based on the United States Geological Survey solute transport code (Konikow and Bredehoeft, 1978) which computes the changes in concentration over time due to advection, dispersion, and mixing. The code solves for flow and transport on a finite-difference grid and progresses through time in a discrete, time-stepping manner. Within each time step, BIOPLUME II solves solute transport equations for both oxygen and hydrocarbon, and then applies the principle of superposition to simulate the reaction between hydrocarbon and oxygen. This reaction is assumed to be instantaneous based on the assumption that the microflora have acclimated to the contaminant and that the rate of oxygen delivery is much slower than the rate of oxygen consumption by microbes (Rifai et al., 1988). For the purposes of this modeling exercise, it was specified that 3.2 units of oxygen are required to completely biodegrade 1 unit of hydrocarbon (Wiedemeier et al., 1995).

4.8.3 Model Assumptions

To facilitate the numerical methods, the model uses a rectangular, uniformly spaced, block-centred, finite-difference grid, in which nodes are defined at the centres of rectangular cells. Following is a list of the main assumptions made in the development of the flow and solute transport model (Konikow and Bredehoeft, 1978; Borden and Bedient, 1986b). They should be considered when evaluating the model predictions.

1. Darcy's law is valid and hydraulic head gradients are the only significant driving mechanism for fluid flow.
2. The porosity and hydraulic conductivity of the aquifer are constant with time, and porosity is uniform in space.
3. Gradients of fluid density, viscosity, and temperature do not affect the velocity distribution.
4. Ionic and molecular diffusion are negligible contributors to the total dispersive flux.
5. Vertical variations in head and concentration are negligible.
6. The aquifer is homogeneous and isotropic with respect to longitudinal and transverse dispersivity.
7. Where oxygen transport is rate limiting, the biological processes of biodegradation can be approximated as an instantaneous reaction.

Given the conditions at the site, these assumptions are deemed suitable for simulating intrinsic bioremediation at the FFTA. They do, however, limit the accuracy of the model prediction. In particular, the assumption that vertical variations in concentration were negligible required that the point measurements of concentration in wells with short screened intervals be averaged over the assumed depth of the aquifer. At this time, there is no accurate estimate of the thickness of the lower sand aquifer, so a thickness of 4.6m was assumed (as discussed in Section 4.8.4.5).

4.8.4 Model Input

The model requires a number of physical parameters to describe the flow and transport characteristics of the system. Boundary conditions for hydraulic head and background

concentration and the initial contaminant concentrations are also required to define the model simulation. The parameters entered into the model are summarized below. Parameters that were varied during the calibration process are indicated.

4.8.4.1 Boundary Conditions

An 11x12 cell grid was established with cell dimensions of 30.5 x30.5m (100 x 100 feet) as shown in Figure 20. This grid encompassed the entire plume and provided adequate space to display different plume configurations. The program requires that a no-flow outer boundary surround the entire modeling area. Constant head inner boundary conditions were applied just inside the upgradient and downgradient edges. Hydraulic heads in these cells were specified to approximate site conditions (see Appendix J for model input data). Diffuse groundwater recharge (i.e. infiltration) from surface was not considered to add a significant amount to the flow system due to the overlying clay till layer.

4.8.4.2 Effective Porosity

The uniform value of effective porosity was assumed to be 0.3 and was not varied during model calibration. This is a typical value for a silty sand aquifer (Freeze and Cherry, 1979). Sensitivity analysis carried out on other BIOPLUME II models suggests that models are not sensitive to reasonably small changes in porosity (Rifai et al., 1988).

4.8.4.3 Dispersivity

Dispersion refers to the process whereby a plume will spread out in a longitudinal direction (along the direction of groundwater flow) and the transverse direction (perpendicular to groundwater flow). Dispersivities are commonly estimated empirically based on the size of the plume (Freeze and Cherry, 1979). The longitudinal dispersivity was initially set to 3.3m (10 feet), and was not varied during model calibration. Transverse dispersivity was estimated as one tenth of the longitudinal dispersivity and also not varied during model calibration. The calibrated model was found not to be sensitive to variations in this parameter (see Section 4.8.6).

4.8.4.4 *Coefficient of Retardation*

As discussed in Section 4.5.4, the retardation factor (R) for the entire aquifer was estimated to be 1.3. This value was not altered during calibration of the model and sensitivity analysis indicated that the calibrated model was not sensitive to variations in this parameter (see Section 4.8.6).

4.8.4.5 *Transmissivity*

The transmissivity (T) is a lumped flow parameter that reflects both the thickness (b) and the hydraulic conductivity (k) of the aquifer by the relationship:

$$T = kb \qquad [28]$$

where: T = transmissivity (length^2/time)

k = hydraulic conductivity (length/time)

b = aquifer thickness (length)

In BIOPLUME II, transmissivity values can be assigned to each node in the grid and are entered as an input array. In order to calibrate the model hydraulic head values to closely match those measured in the field, the transmissivity values were varied in lines and blocks in a trial-and-error fashion. The intent was to obtain a flow pattern from the model that simulated the flow pattern observed in the field. To simplify the calibration procedure, the aquifer thickness was assumed to be a constant, uniform over the aquifer at 4.6m (15 feet). This forced the model to adjust the hydraulic conductivity values for each cell when calculating a flow solution. The calculated values of k were included as model output (Appendix J) and compared well with the hydraulic conductivity estimated for the aquifer as a whole of $1x10^{-4}$ m/s, as discussed in Section 4.5. The true picture in the subsurface likely lies somewhere in between; changes in thickness and hydraulic conductivity across the aquifer will, combined, cause the pattern of hydraulic head measured across the modeled area.

4.8.4.6 *Dissolved Oxygen Levels*

Dissolved oxygen was made available for biodegradation of the contamination from three separate sources in the computer model. Initial levels of DO in the aquifer (at t=0) were set to 4

mg/L. This parameter is unlikely to influence the groundwater conditions at the time of interest, 40 years from the beginning of the simulation. The oxygen concentration for uncontaminated groundwater entering the system from upgradient was set to 4.5mg/L to reflect background levels measured in HP-4 and HP-16. This level is significantly lower than 12mg/L, the saturation value for dissolved oxygen in water at 8°C. Because of the clay till layer above the aquifer, diffuse reaeration of the aquifer from above was considered to contribute a small amount of dissolved oxygen to each cell, by applying a first order hydrocarbon decay rate of 0.00055 day^{-1}. Holder *et al.* (1999) suggest that reaeration of oxygen to O_2 depleted aquifers is an important physico-chemical process that has been too often overlooked in contaminant modeling exercises. This small amount was selected however, because the overlying clay till layer would inhibit the oxygen recharge. This rate can be considered analogous to an aerobic biodegradation rate due to the model assumption of instantaneous reaction between oxygen and hydrocarbon. Given the much higher first order aerobic biodegradation rates measured in the laboratory with contaminated samples from the aquifer, this parameter can be considered a conservative estimate that reflects the limited capacity for dissolved oxygen recharge at the site.

4.8.4.7 Anaerobic Degradation Coefficient

Anaerobic degradation is accounted for in BIOPLUME II by applying a first order decay constant to the hydrocarbon concentration. As outlined in Section 4.6.4, anaerobic biodegradation is believed to account for approximately 95% of the total BTEX degraded. The anaerobic degradation coefficient was used to calibrate the model with the caveat that the ratio of aerobic to anaerobic degradation was maintained and the value fell within the published literature range of 0.007 - 0.19 day^{-1} (Wiedemeier et al., 1995).

4.8.4.8 Source Concentration and Distribution

In order to simulate the diffuse leakage of dissolving hydrocarbon into the aquifer below the training area, contaminant source "injection wells" were included at three nodes in the model grid. The program treats these contaminant sources as instantaneously mixed over the cell area, so high concentrations and low volumetric flows were applied to the wells in order not to affect the

groundwater flow prediction through the cell. This contaminant loading in each of the three cells was adjusted to calibrate the output to match the observed behaviour.

4.8.5 Model Calibration

The flow model was calibrated first by adjusting the transmissivity (T) of the aquifer until the predicted pattern of hydraulic head across the modeled area closely matched the expected pattern. The predicted contaminant plume was then adjusted to match conditions present in the field today, 40 years after the beginning of the simulation. This was accomplished by manipulating the contaminant injection sources, the coefficient of reaeration, and the anaerobic biodegradation coefficient.

4.8.5.1 Groundwater Flow Calibration

In order to simulate the decreasing head loss with distance (dH/dl) downgradient of the source area (Figure 5) the transmissivity (T) of the aquifer was manipulated through trial-and-error adjustment. This process was iterated until the head distribution output by the groundwater flow model resembled the current field conditions. A priority was placed on matching the direction of groundwater flow through the source area and immediately downgradient of the source. The model hydraulic heads are plotted as a contour map included as Figure 21.

The groundwater flow model error was quantified by calculating the root mean squared error (RMS) between the measured and simulated head levels.

$$RMS = \left[\frac{1}{n}\sum_{i=1}^{n}(H_m - H_s)_i^2\right]^{0.5} \qquad [29]$$

Where: n = number of points where heads were compared

H_m = measured head value (interpreted from head contour map)

H_s = simulated head value (model output)

An RMS error of 0.12m (0.41 feet) over 76 calibration points was achieved. This represents a calibration error of 5.1% given the head loss over the grid is 2.4m (8 feet). A plot of measured vs. calibrated heads, included as Figure 22, shows good agreement between the two data sets and

exhibits a tight and randomly scattered error pattern, which supports the validity of the groundwater flow model.

4.8.5.2 Contaminant Transport Calibration

The dissolved hydrocarbon transport component of the model was then adjusted until the model plume reflected the field measurements of contamination concentrations. This was achieved by adjusting the source concentrations and the biodegradation parameters. Because a 2-D plan view model was used, the concentration values at a node represent the average concentration over the entire depth of the aquifer within a cell. Thus, during calibration, consideration was given to the varying character of the field measurements. The concentration of hydrocarbons in monitoring wells with long screened intervals was likely diluted with uncontaminated groundwater from other depths in the aquifer. HydroPunch samples, in contrast, sample a discrete interval of the aquifer and may reflect a comparatively elevated level of contamination should a peak zone with depth be intercepted (i.e., near the water table).

A complete summary of the final calibrated model input is included as Appendix J. The contaminant and dissolved oxygen contours of the calibrated model are shown as Figures 23 and 24, respectively.

4.8.6 Sensitivity Analysis for Calibrated Model

To investigate the robustness of the model, selected parameters were independently adjusted over a reasonable range of values and the variability of model output evaluated. This was accomplished by plotting the predicted hydrocarbon concentration along the plume centreline. Results of the sensitivity analysis are included as Figures 25 through 30. The parameters that had little influence on the shape of the contaminant plume were the retardation coefficient, and the longitudinal and transverse dispersivity. It was discovered that the model is most sensitive to changes in the biodegradation parameters (coefficient of reaeration, and the coefficient of anaerobic decay) and the hydraulic conductivity of the media. These results are similar to the findings of Rifai, *et al.* (1988) who analyzed the sensitivity of a BIOPLUME II model to the same set of parameters.

To examine the influence of the biodegradation parameters on the model, the first order decay coefficients of reaeration and anaerobic decay were varied together, as they have the same mathematical influence on the model prediction. The reaeration coefficient was varied by an order of magnitude above and below the model prediction, and the anaerobic decay coefficient was varied between a minimum of 0.007 d^{-1} and a maximum of 0.19 d^{-1}. The anaerobic decay range was selected from the extremes of published literature values on field data as summarized in Wiedemeier *et al.*, 1995. As shown in Figure 28, when the biodegradation parameters are set to the high end of the range, contaminant levels are only present in the cells serving as contaminant source. When biodegradation parameters are set to the low end of the range, the concentration and size of the contaminant plume dramatically increase.

The transmissivity was varied uniformly across the input array by an order of magnitude and the thickness of the aquifer was kept constant. This forced the hydraulic conductivity calculated by the program to increase by the same magnitude. The results of this analysis are compared on Figure 29, which shows the BTEX concentration plotted along the plume centreline. At high conductivities, the model plume was flushed with a higher volume of dissolved oxygen, which caused a significant decrease in contaminant concentration. The leading edge of the plume contained a lower concentration of contaminant, which was instantly biodegraded. At low conductivity the plume concentration at the source is nearly double that of the expected plume due to the slower overall migration rate.

4.8.7 Model Predictions

The calibrated model was run with contaminant input from the source for intervals of 25, 40 and 80 years (Figure 30). This simulates the scenario of a continuous dissolved hydrocarbon source with no decline in source concentration. The hydrocarbon plume output remained constant, indicating that the plume had reached steady state conditions. This suggests that the plume will not increase in size or concentration in the future. Indeed, with the excavation and removal of the contaminant source, the plume should decrease in size and magnitude until bioremediation is complete.

To test this scenario, the model was run with the existing contaminant conditions as input (both DO and hydrocarbon) and no source input. The model predicts that the plume will rapidly decrease in size and be completely bioremediated within one year (Figure 31). This prediction is non-conservative, as complete removal of source hydrocarbon was not likely achieved. The pattern of plume biodegradation remains the same whether the source is completely removed or if the source is reduced to a small residual that slowly decays. The length of time remaining until the plume is completely degraded depends on a variety of factors. Some of these are: the amount of residual hydrocarbon contamination left in and around the excavated pit, the source decay rate (including evaporation and weathering), biodegradation of hydrocarbon contamination in the vadose zone, and the reduced rate of biodegradation occurring at low hydrocarbon concentrations when substrate bioavailability becomes an issue. The model prediction for the dissolved oxygen concentration (Figure 32) reveals that the depleted DO levels will take approximately 10 years to approach background levels after source removal.

4.8.8 Summary of Model Results

Modeling of the site was carried out with a two-dimensional finite difference numerical computer model. Sensitivity analysis suggests that this is a fairly robust model, as only the biodegradation rate and the hydraulic conductivity estimates significantly influence the predictions. These estimates are reasonably well defined and are limited in range due to calibration with field data. Model results indicate that the contaminant plume has reached steady state conditions, and with the removal of the contaminant source at the site, the plume should dramatically and quickly reduce in size until it is completely bioremediated.

4.9 Closure

In order to address weaknesses in the current site model, some additional field investigation is recommended. A simple supplementary site investigation should provide enough information to confirm the expected contaminant migration behaviour. Once this model has been confirmed, a series of point of compliance monitoring wells should be installed downgradient of the existing hydrocarbon plume. The groundwater in these wells, and in selected monitoring

wells within the plume, should be sampled on an ongoing basis to confirm the plume is decreasing in concentration and size.

4.9.1 Supplementary Site Investigation

As discussed in Section 4.6.2, a follow up site investigation is recommended to the southeast of the excavated pit at the site. The intent of this work is to confirm the geologic and hydrogeologic model for the site and to obtain groundwater samples from the lower sand layer to be analyzed for BTEX contamination. A solid stem auger hole and three HydroPunch® test holes should be adequate to obtain the required information. The recommended location and depth for the test holes is shown on Figure 33.

By advancing the auger hole first, the depth to the top of the lower sand layer and the water table within it can be confirmed. A soil sample for BTEX analysis should not be required unless there are obvious indications of hydrocarbon contamination. The proposed HydroPunch® hole depths could then be adjusted to ensure they are near the top of aquifer where BTEX concentration levels should be highest.

It is important that the groundwater level be measured in each HydroPunch® hole once the level has been allowed to fully recharge. Groundwater level measurements should also be obtained in all other monitoring wells at the site during the same investigation in order to confirm the groundwater flow model.

Should any BTEX be discovered in samples from any of these locations, consideration should be given to generating a new computer model of the site to provide an improved prediction of the future contaminant plume configurations.

4.9.2 Long Term Monitoring

In order to confirm the prediction of contaminant modeling and ensure that the plume migration behaviour is as expected, the installation of four monitoring wells downgradient of the source area is recommended. The proposed location of these wells is shown on Figure 34, and is dependent on the confirmation of the site model by the supplementary site investigation (i.e. no contaminants discovered to the southeast of the contaminant source). The wide north-south

spread of the wells is required in order to ensure that all possible contaminant migration pathways are likely intercepted by the wells. They are located sufficiently far downgradient that no dissolved contamination should intersect the wells, but close enough not to be impacted by other potential undiscovered contaminant sources. The wells should be screened just below the water table within the lower sand unit as prescribed on Figure 34. Should conductive sandy layers be encountered with evidence of hydrocarbon contamination at depths shallower than suggested, the well should be screened over that interval and further site investigation pursued. If the water table appears to be confined within the lower sand layer, then it is important that the well screen intercept the sand in order to maintain a hydraulic connection.

In order to confirm the decline in the plume concentration with time, the groundwater from two existing wells on the site should be sampled for BTEX concentration. MW-01 (installed August 1998) and MW-L (installed by EBA Engineering Consultants, February 1998) will serve this purpose. Installation details of these monitoring wells are described in Table 8.

For the first few years, quarterly sampling of these wells could be carried out to demonstrate temporal consistency in groundwater concentrations of the contaminant plume. Beyond this time, annual sampling of the groundwater in these wells should be sufficient to confirm the model predictions. Contaminant levels in these wells should be approximately equal to current levels as listed below:

Monitoring Well	Benzene ug/L	Toluene ug/L	Ethylbenzene ug/L	Xylenes ug/L
MW-01	220	0.96	140	<0.5
MW-L	1400	37	460	2700

4.10 Summary for Fire Fighter Training Area

1) A low level of dissolved phase hydrocarbon contamination is present in the lower aquifer on the site with measurable concentrations of BTEX in the groundwater. Some residual contamination is also present, although most of the source has been removed.

2) Evidence for intrinsic bioremediation of contamination includes:

- rapidly decreasing dissolved contaminant concentration levels downgradient.
- geochemical evidence of depleted terminal electron acceptors (TEAs) and enriched products of microbial degradation in the groundwater across the site.
- enumeration of significant populations of: total heterotrophic, nitrate/nitrite reducing, iron reducing and JP-4 degrading microbes.
- microorganisms in soil from the contaminated area exhibit the capacity to biodegrade aromatic hydrocarbon under cold temperature conditions

3) Modeling of the contaminant plume suggests that a steady state has likely been achieved. The removal of the source hydrocarbon contamination will dramatically reduce the time for complete bioremediation of the site. The maximum extent of the plume based on sampling and analysis has been demonstrated to be approximately 75m downgradient of the excavation. This corresponds reasonably well in the calibrated model (80m) when expected values of parameters are used.

4) Results suggest that the capacity for intrinsic bioremediation is sufficient to adequately serve as the final remedial approach given the following:
   - potential groundwater contamination is investigated in the lower sand aquifer to the southeast of the FFTA and results conform to predicted behaviour.
   - ongoing monitoring of the contaminant levels is continued to ensure the contaminant migration pattern is as expected.

Table 5: Groundwater Sample Preservation Summary

Analyte	Container Volume and Type	Preservative
BTEX/TEH*/TVH	250 ml amber glass	0.2g ascorbic acid 0.5ml 1:1 hydrochloric acid
Complete VOC trace **	40 ml glass	sodium thiosulfate
Routine *** (NO_3, NO_2, SO_4)	500 ml polyethylene	None
Sulfide	100 ml polyethylene	1 ml zinc acetate 1 ml 6N sodium hydroxide
Ferrous Iron	40 ml glass	0.5 ml 6N hydrochloric acid
Methane	40 ml glass	0.1 ml 6N hydrochloric acid

*TEH = Total Extractable hydrocarbons, TVH = Total Volatile Hydrocarbons
**VOC = Volatile Organic Compounds
***Routine analysis included: bicarbonate, calcium, carbonate, conductance, hardness, hydroxide, magnesium, pH, potassium, sodium, total dissolved solids, and total alkalinity.

Table 6: Details of Water Levels, Monitoring Wells and HydroPunches®

Details for all wells and August 1998 Measurements

Hole I.D.	Northing	Easting	Top of Pipe* Elev. m	Depth to Screened Interval** m	Aug 6,1998 Depth to water m	Aug 6,1998 Water Elev. masl	Comments
M (4-08)	6029800.924	546374.349	540.082	6.5-8.5	5.597	534.485	
I	6029901.396	546321.629	540.021	?-4.8	3.458	536.563	
MW-01	6029866.887	546408.731	540.141	5.2-5.9			
L (EBA15)	6029863.340	546381.094	540.807	4.5-8.2	5.986	534.821	
K (EBA16)	6029838.154	546384.850	540.469	4.5-8.2	5.655	534.814	
P(1-08)	6029733.875	546322.786	539.473	3.0-5.5	4.507	534.966	
HP-1	6029863.051	546396.551	539.582	8.5-9.1			
HP-2	6029841.053	546414.305	539.463	5.2-5.8	4.985	534.478	
HP-3	6029866.391	546457.671	538.922	5.5-6.1	4.245	534.677	
HP-4	6029753.772	546282.182	539.077	6.4-7.0	4.06	535.027	
HP-16	6029784.269	546261.187	539.007	6.4-7.0			
HP-17	6029913.108	546433.639	539.165	8.5-9.1			
HP-18	6029957.210	546410.508	539.341	10.1-10.7			
HP-19	6029988.893	546391.667	539.575	9.1-10.7			
HP-20	6029980	546382	539.56	2.1-2.7			

Additional Measurements June 1998

Hole I.D.	Northing	Easting	Top of Pipe* Elev. m	Depth to Screened Interval** m	June 16,1998 Depth to water m	June 16,1998 Water Elev. masl	Comments
M (4-08)	6029800.924	546374.349	540.082	6.5-8.5	5.568	534.514	
L (EBA15)	6029863.340	546381.094	540.807	4.5-8.2	6.125	534.682	
K (EBA16)	6029838.154	546384.850	540.469	4.5-8.2	5.795	534.674	

Additional Measurements October 1998

Hole I.D.	Northing	Easting	Top of Pipe* Elev. m	Depth to Screened Interval** m	Oct 2/7,1998 Depth to water m	Oct 2/7,1998 Water Elev. masl	Comments
M (4-08)	6029800.924	546374.349	540.082	6.5-8.5	5.694	534.388	
MW-01	6029866.887	546408.731	540.141	5.2-5.9	5.34	534.801	
L (EBA15)	6029863.340	546381.094	540.807	4.5-8.2	6.408	534.399	
K (EBA16)	6029838.154	546384.850	540.469	4.5-8.2	5.717	534.752	
HP-17	6029913.108	546433.639	539.165	8.5-9.1	< 4.6	> 534.565	not fully recharged
HP-18	6029957.210	546410.508	539.341	10.1-10.7	9.5-10.2	529.8-529.1	water level below top of screen
HP-19	6029988.893	546391.667	539.575	9.1-10.7	< 4.9	> 534.675	not fully recharged
HP-20	6029980	546382	539.56	2.1-2.7	1.33	536.25	shallow aquifer, 1 m from HP-19

*Ground surface for Hydropunches
** From top of pipe

Table 7: FFTA Groundwater Parameters Measured in the Field

Monitoring Well	Screened Interval (m)	Date	DO mg/L	Temp °C	pH	Conductivity uS/cm	Redox Potential mV
MW-K (EBA-15)	4.5-8.2	Aug	2.3	10.6*	7.1	1000	-41
MW-L (EBA-16)	4.5-8.2	Aug	0.7	9.1*	7.3	688	-40
MW-M (4-08)	6.5-8.5	Aug	0.9	7.5*	7.4	560	
MW-01	5.2-5.9	Oct		8.3*			
HP-02	5.2-5.8	Aug	1.4	14	6.9	834	-35
HP-03	5.5-6.1	Aug	0.8	13	6.9	515	-37
HP-04	6.4-7.0	Aug	5.3	14	8.0	616	-38
HP-16	6.4-7.0	Oct	1.2	8	7.8	300	
HP-17	8.5-9.1	Oct	1.1	10	7.9	380	
HP-19	9.1-10.7	Oct	0.8	11	7.9	405	
HP-20**	2.1-2.7	Oct	6.9	12	6.9	125	

* Measured October 1-8, 1998 with downhole temperature transducer
** Shallow aquifer

TABLE 8: Chemical Analysis of Groundwater (A,B) and Soil (C) from the Fire Fighter Training A

8A Groundwater Contaminants

Hole I.D. units Detection Limit	Location	Date (1998)	Sampling Method*	Screened Interval (m)	Benzene ug/L [ppb]	Toluene ug/L [ppb]	Ethylbenzene ug/L [ppb]	Xylenes ug/L [ppb]	Total BTEX ug/L [ppb]
HP-4	upgradient	Aug	waterra	6.4-7.0					
HP-16	upgradient	Oct	waterra	6.4-7.0	<0.5	<0.5	<0.5	<0.5	<0.5
HP-16(dup)	upgradient	Oct	waterra	6.4-7.0	<0.5	<0.5	<0.5	<0.5	<0.5
MW-L (EBA15	near source	Aug	bladder	4.6-8.2	1400	37	460	2700	4597
MW-K(EBA16	near source	Aug	bladder	4.6-8.2	12	<0.05	17	14	43
MW-M(4-08)	near source	June	bladder	6.4-8.5	2.2	18	2.2	27	49.4
MW-M(4-08)	near source	Oct	bladder	6.4-8.5	0.9	<0.5	<0.5	<0.5	0.9
MW-I	near source	June	bladder	?-4.8	<0.5	<0.5	0.5	<0.5	0.5
MW-01	downgradient	Oct	bladder	5.2-5.9	220	0.96	140	430	790.96
HP-1	downgradient	Aug	waterra	8.5-9.1	<0.5	0.5	<0.5	<0.5	0.5
HP-2	downgradient	Aug	waterra	5.2-5.8	380	1.6	170	540	1091.6
HP-3	well downgradien	Aug	waterra	5.5-6.1	0.6	<0.5	<0.5	0.8	1.4
HP-17	well downgradien	Oct	waterra	8.5-9.1	<1	<1	<1	<1	<1
HP-18	well downgradien	Oct	waterra	10.1-10.7	<1	<1	<1	<1	<1
HP-19	well downgradien	Oct	waterra	9.1-10.7	<0.5	<0.5	<0.5	<0.5	<0.5
HP-20	well downgradien	Oct	waterra	2.1-2.7	<0.5	<0.5	<0.5	<0.5	<0.5

8B Groundwater All Other Analyses

Hole I.D. units Detection Limit	Location	Date (1998)	Sampling Method*	Screened Interval (m)	Nitrate/nitrite mg/L [ppm] 0.05	Ferrous Iron mg/L [ppm] 0.1	Sulfate mg/L [ppm] 0.5	Sulfide mg/L [ppm] 0.002	Methane mg/L [ppm] 0.1	Total Alk mg/L [ppm] 5	TOC mg/L [ppm] 1
HP-4	upgradient	Aug	waterra	6.4-7.0	<0.05	68.0	11.1	<0.002	0.0	173	4
HP-16	upgradient	Oct	waterra	6.4-7.0	<0.05	68.4	12.5	<0.002		159	
HP-16(dup)	upgradient	Oct	waterra	6.4-7.0							
MW-L (EBA15	near source	Aug	bladder	4.6-8.2	<0.2	44.4	7.6	<0.002	7.4	529	
MW-K(EBA16	near source	Aug	bladder	4.6-8.2	<0.05	21.7	18.6	<0.002	0.8	346	
MW-M(4-08)	near source	June	bladder	6.4-8.5							
MW-M(4-08)	near source	Oct	bladder	6.4-8.5	<0.05	0.6	11.2	<0.002		276	
MW-I	near source	June	bladder	?-4.8							
MW-01	downgradient	Oct	bladder	5.2-5.9	<0.05	23.2	8.8	0.004		364	
HP-1	downgradient	Aug	waterra	8.5-9.1	<0.05	55.0	9.7		0.3	337	9
HP-2	downgradient	Aug	waterra	5.2-5.8	<0.05	85.5	4.1	0.121	6.3	392	
HP-3	well downgradien	Aug	waterra	5.5-6.1	0.06	48.8	5.5	0.099	0.2	268	5
HP-17	well downgradien	Oct	waterra	8.5-9.1	<0.05	253.0	4.2	0.006		176	
HP-18	well downgradien	Oct	waterra	10.1-10.7				0.005			
HP-19	well downgradien	Oct	waterra	9.1-10.7	<0.05	307.0	7.0	0.005		170	
HP-20	well downgradien	Oct	waterra	2.1-2.7	0.06	4.8	3.4	<0.002		59	

*Method
bladder positive displacement bladder pump
waterra waterra pump

TABLE 8: Chemical Analysis of Groundwater (A,B) and Soil (C) from the Fire Fighter Training Area

8C Soil Contaminants

Hole I.D. units Detection Limit	Location	Date (1998)	Sampling Method*	Depth	Benzene ug/g (ppm) 0.01	Toluene ug/g (ppm) 0.01	Ethylbenzene ug/g (ppm) 0.01	Xylenes ug/g (ppm) 0.01	TEH ug/g (ppm) 5	TVH ug/g (ppm) 0.5
MW-01	downgradient	Aug	Split S	5.49	<0.01	<0.01	<0.01	<0.01	17	3.6
AH-21	downgradient	Oct	Solid S	4.60	<0.01	<0.01	<0.01	<0.01		

*Method

Split S Disturbed sample from split spoon sampler (3-3/8" ID)

Solid S Disturbed sample from 6" solid stem auger

Table 9: FFTA Mass Ratio Summary of TEA Consumed or Metabolic Byproduct Produced to Total BTEX Degraded

Terminal Electron Accepting Process	Mass of BTEX Degraded per unit mass of Electron Acceptor Utilized* (mg)	Mass of BTEX Degraded per unit mass of metabolic Byproduct Produced* (mg)	Measured Concentration Change at the site (mg/L)	Biodegradation Capacity (mg/L)
Aerobic Respiration	0.32		1.5	0.48
Denitrification	0.21		0	0.00
Iron III Reduction		0.05	20	0.92
Sulfate Reduction	0.21		6	1.28
Combined Capacity				2.68
Methanogenesis**		1.28	7.4	9.49

* after Wiedemeier et al, 1995

**assumed total biodegradation capacity

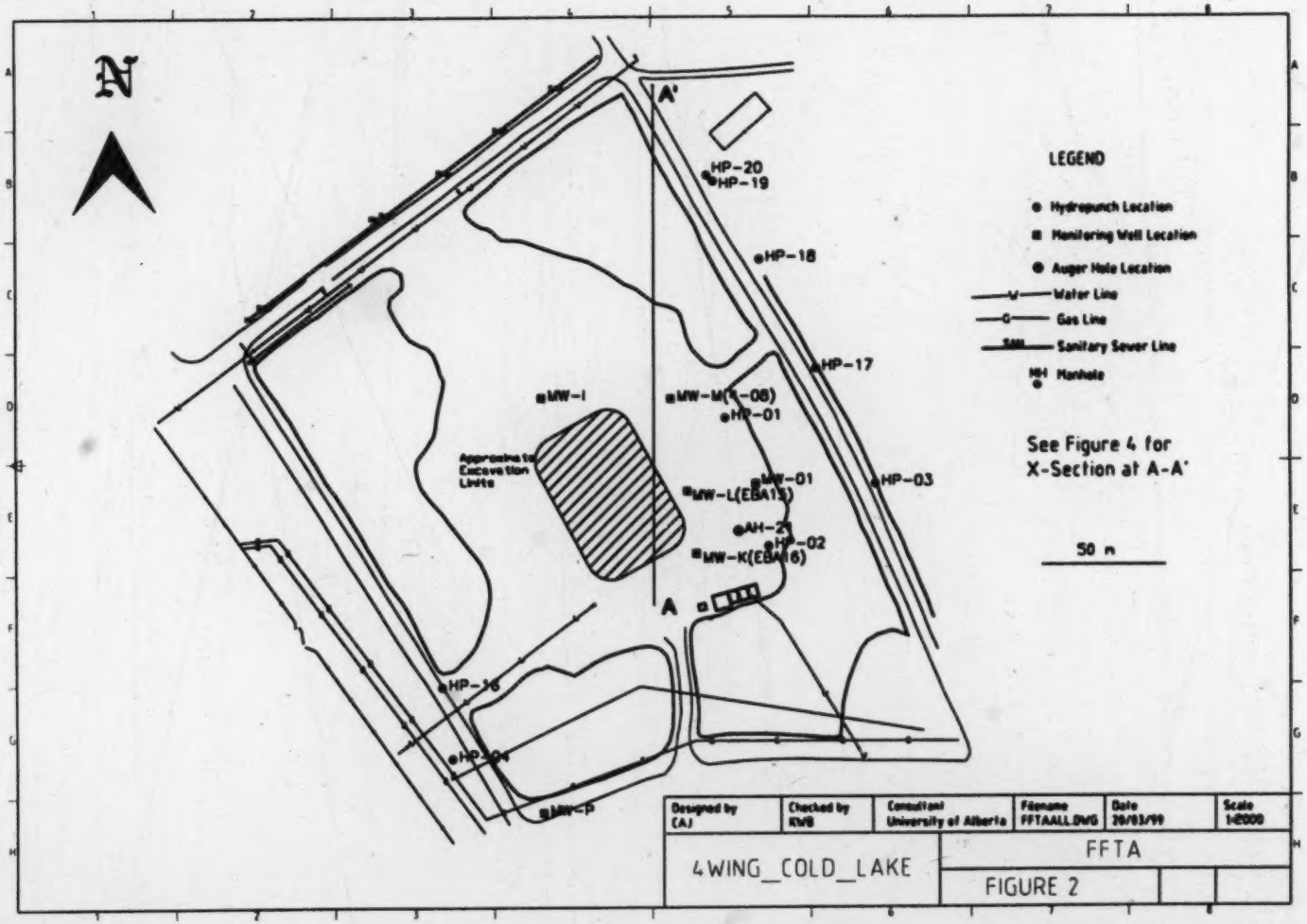
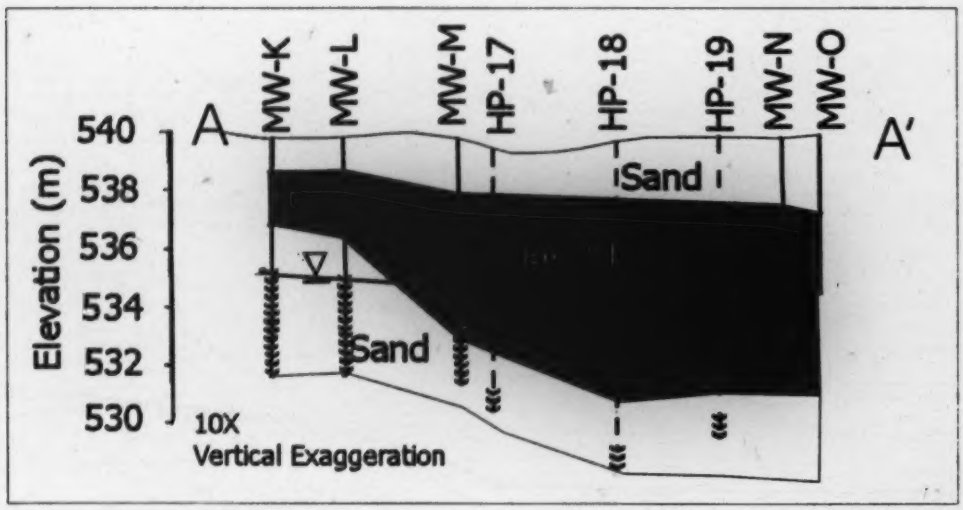

N
A'
A
HP-20
HP-19
HP-18
HP-17
HP-03
HP-02
HP-16
MW-I
MW-M(95-08)
HP-01
MW-01
MW-L(EBA15)
AH-2
MW-K(EBA16)
MW-P
Approximate Excavation Limits
LEGEND
Hydropunch Location
Monitoring Well Location
Auger Hole Location
Water Line
Gas Line
Sanitary Sewer Line
Manhole
See Figure 4 for X-Section at A-A'
50 m
Designed by CAJ
Checked by KWB
Consultant University of Alberta
Filename FFTAALL.DWG
Date 20/03/99
Scale 1:2000
4WING_COLD_LAKE
FFTA
FIGURE 2

Figure 3: Photograph of HydroPunch® Groundwater Sampler

Figure 4: Fire Fighter Training Area Geological Cross Section with North-South Orientation



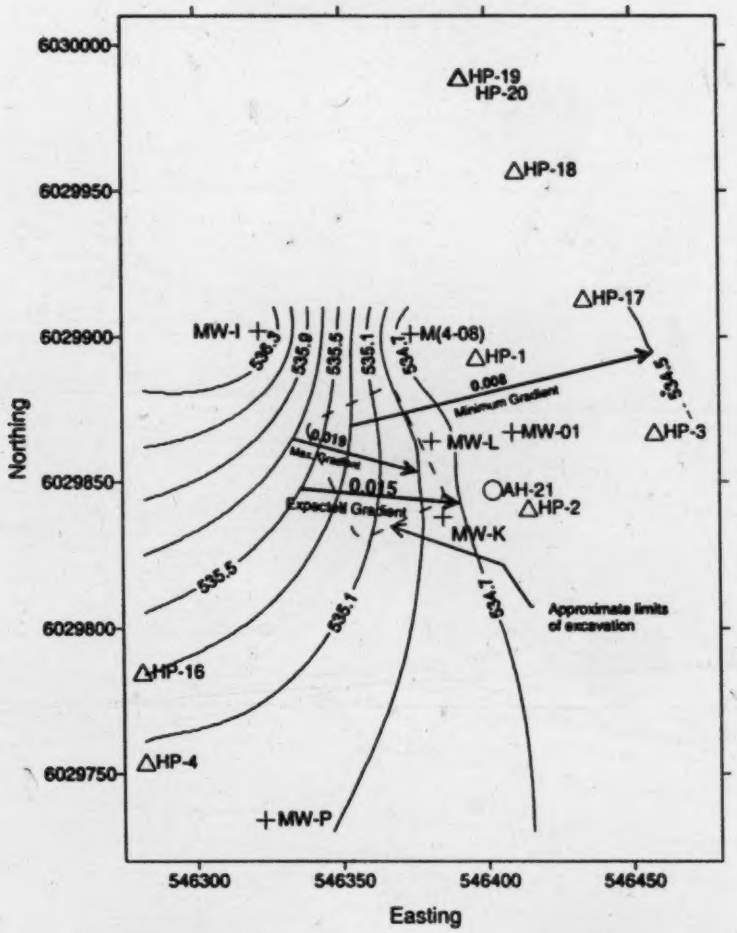
Legend

- Screened Sampling Interval
- Water Table
- HydroPunch Hole
- Monitoring Well

Note: See Figure 2 for location of section in plan view.

Figure 5: Fire Fighter Training Area
Hydraulic Head In Lower Sand Aquifer

AUGUST 1998 (m elevation)



Note: water levels obtained from:
- HP-4
- MW-P
- MW-I
- MW-M (4-08)
- MW-L (EBA 15)
- MW-K (EBA 16)
- HP-3

Auger Hole ○
Monitoring Well +
HydroPunch Hole △

SCALE (m)
0.00 20.00 40.00 60.00 80.00

Figure 6: Fire Fighter Training Area
Groundwater Conductivity Measurements

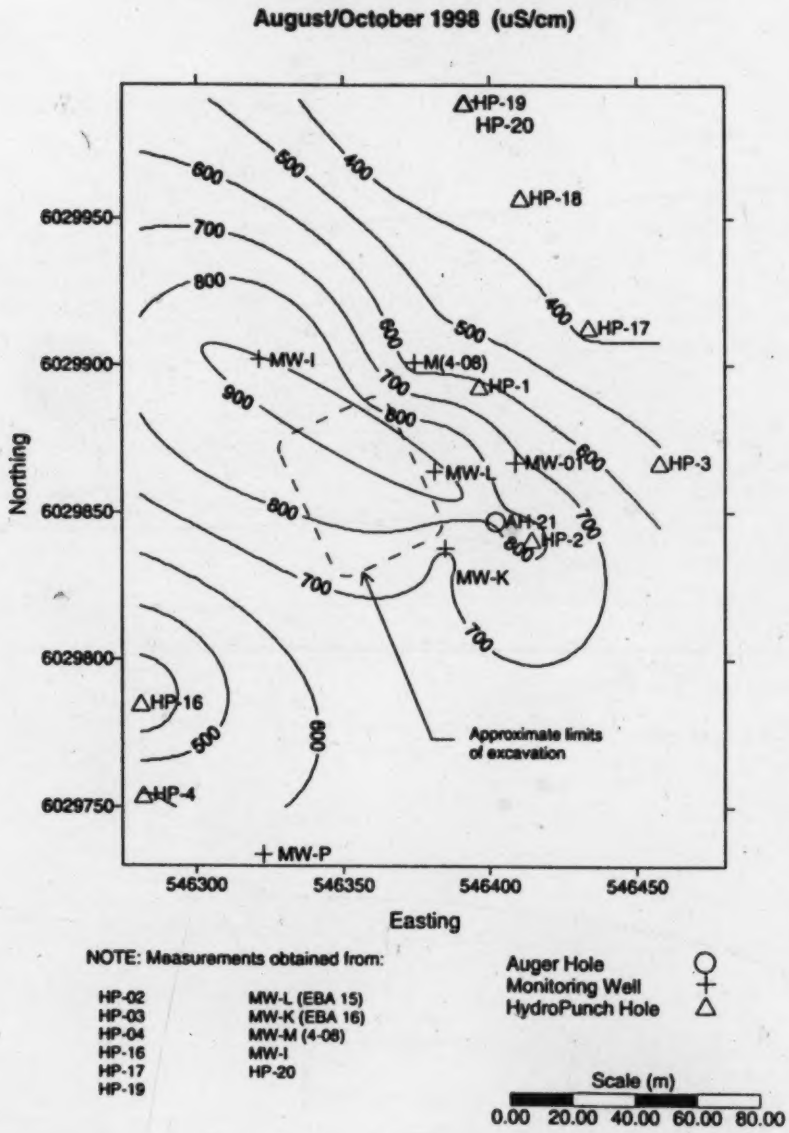


Figure 7: Fire Fighter Training Area
Groundwater Contamination

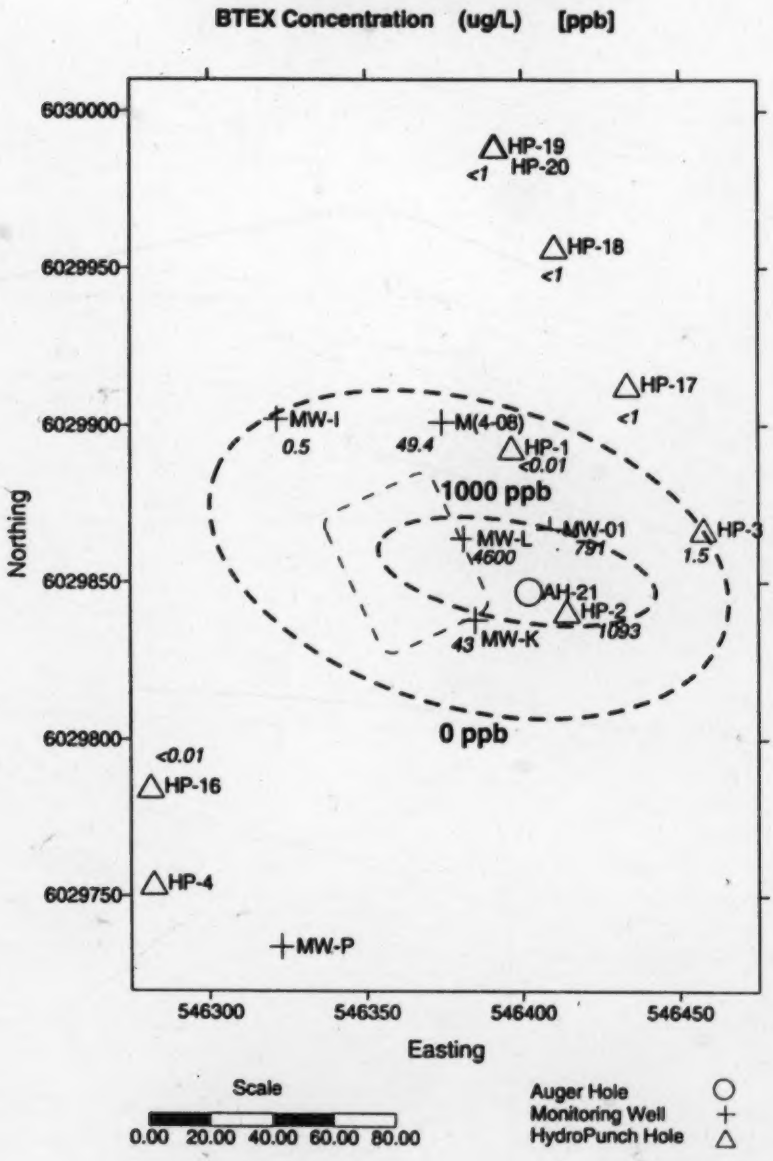
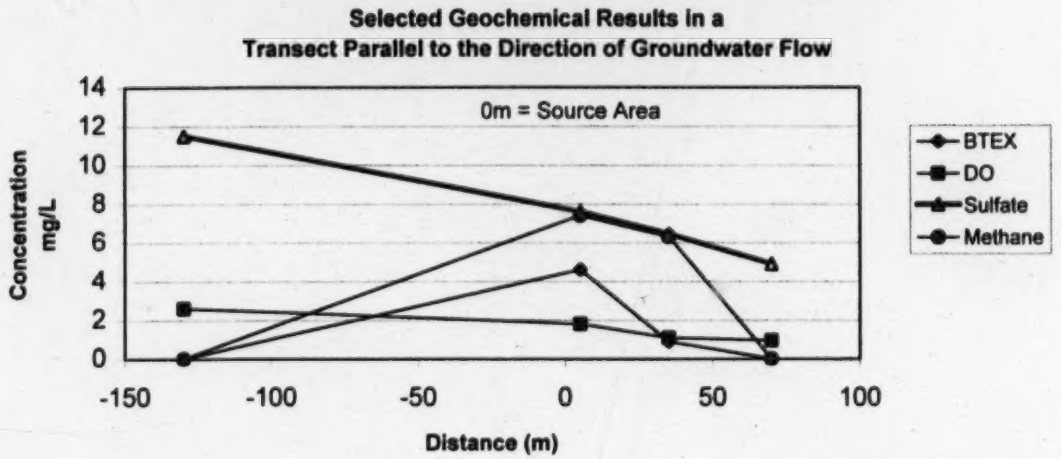


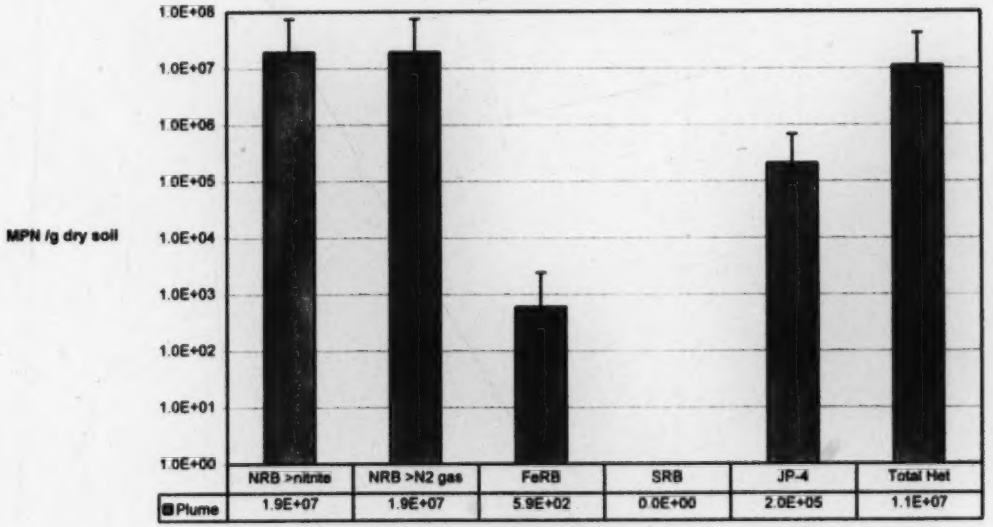
Figure 8: Fire Fighter Training Area Chemistry Results



Location	Monitoring Well	Distance m	BTEX mg/L	DO mg/L	Nitrate mg/L	Sulfate mg/L	Sulfide mg/L	Fe^{2+} mg/L	Methane mg/L
upgradient	HP-16 & HP-18	-130	<0.01	2.6	<0.05	11.5	<0.002	68	<0.1
near source	EBA 15	5	4.6	1.8	<0.05	7.6	<0.002	44.4	7.4
downgradient	AH-1& HP-2	35	0.9	1.1	<0.05	6.5	0.063	54.4	6.3
far downgradient	HP-3 & 17	70	<0.01	0.95	<0.05	4.9	0.08	151	<0.1

Figure 9: FFTA Microbial Enumeration

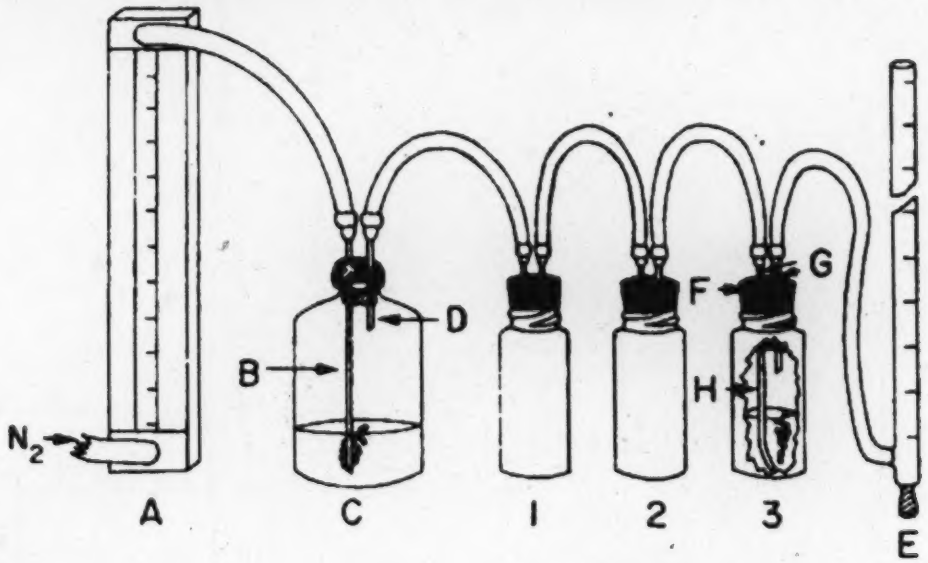
Soil from MW-01 (5.6m depth)
6 weeks Incubation



Error bars at 95% Confidence Interval

NRB>nitrite = Nitrate reducing bacteria that converted nitrate to nitrite
NRB>N2 gas = Nitrate reducing bacteria that converted nitrate to nitrogen gas
FeRB = Iron reducing bacteria
SRB = Sulfate reducing bacteria
JP-4 = JP-4 (jet fuel) degrading bacteria
Total Het = Total Heterotrophic bacteria

Figure 10 Microbial Activity Apparatus (after Fedorak, et al., 1982)



A = Flow Regulator

B = 22 gauge needle to permit bubbling N_2 through acidified mixture

C = Serum vial (125ml or 158ml)

D = 26 gauge needle to permit N_2 to carry CO_2 to liquid scintillation vials

E = Soap Bubble Flowmeter

F = Butyl Rubber Stoppers

G = 26 gauge needles permit inflow/outflow of N_2 gas and CO_2

H = Polyethylene tubing bubbles inflow through $^{14}CO_2$ trapping solution

Figure 11: FFTA Microbial Activity

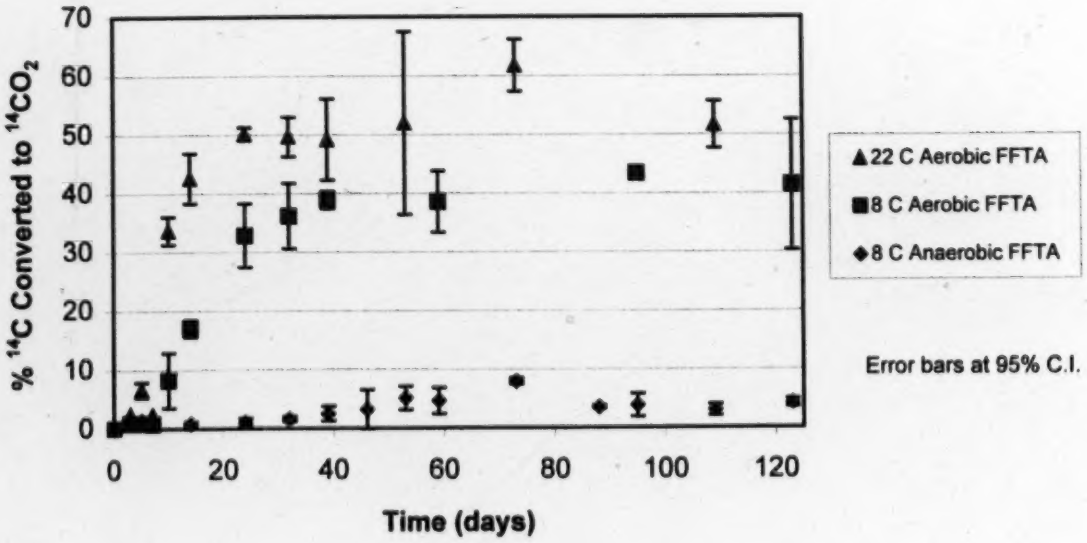
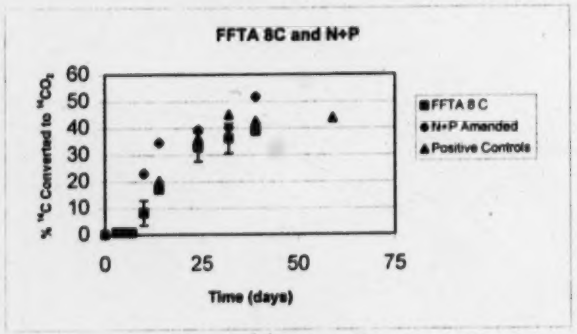
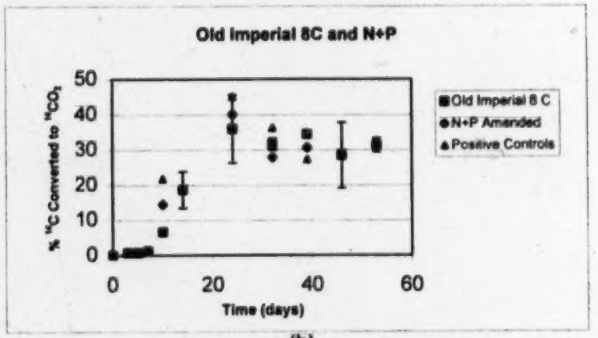


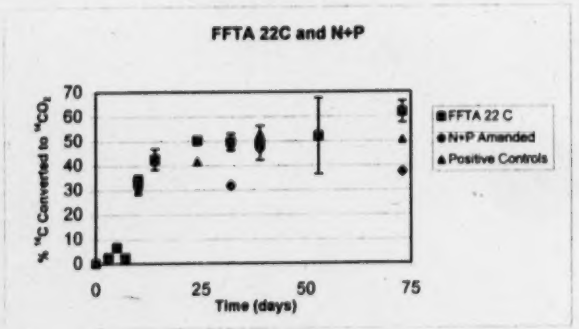
Figure 12
Comparison of Nutrient-Amended Samples, Positive Controls, and Corresponding Unamended Trials for FFTA 8 C (a), Old Imperial 8 C (b), FFTA 22 C (c), and FFTA Anaerobic 8 C (d) samples



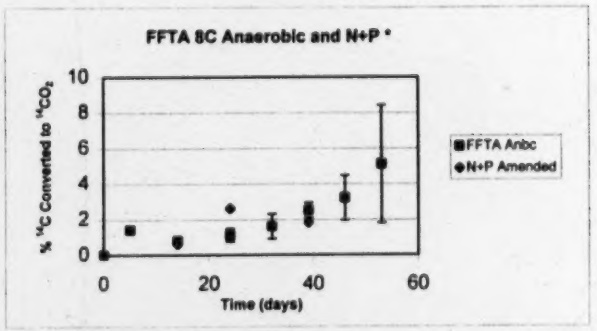
(a)



(b)



(c)



(d)

* Additional unamended sample data to Day 120 not shown

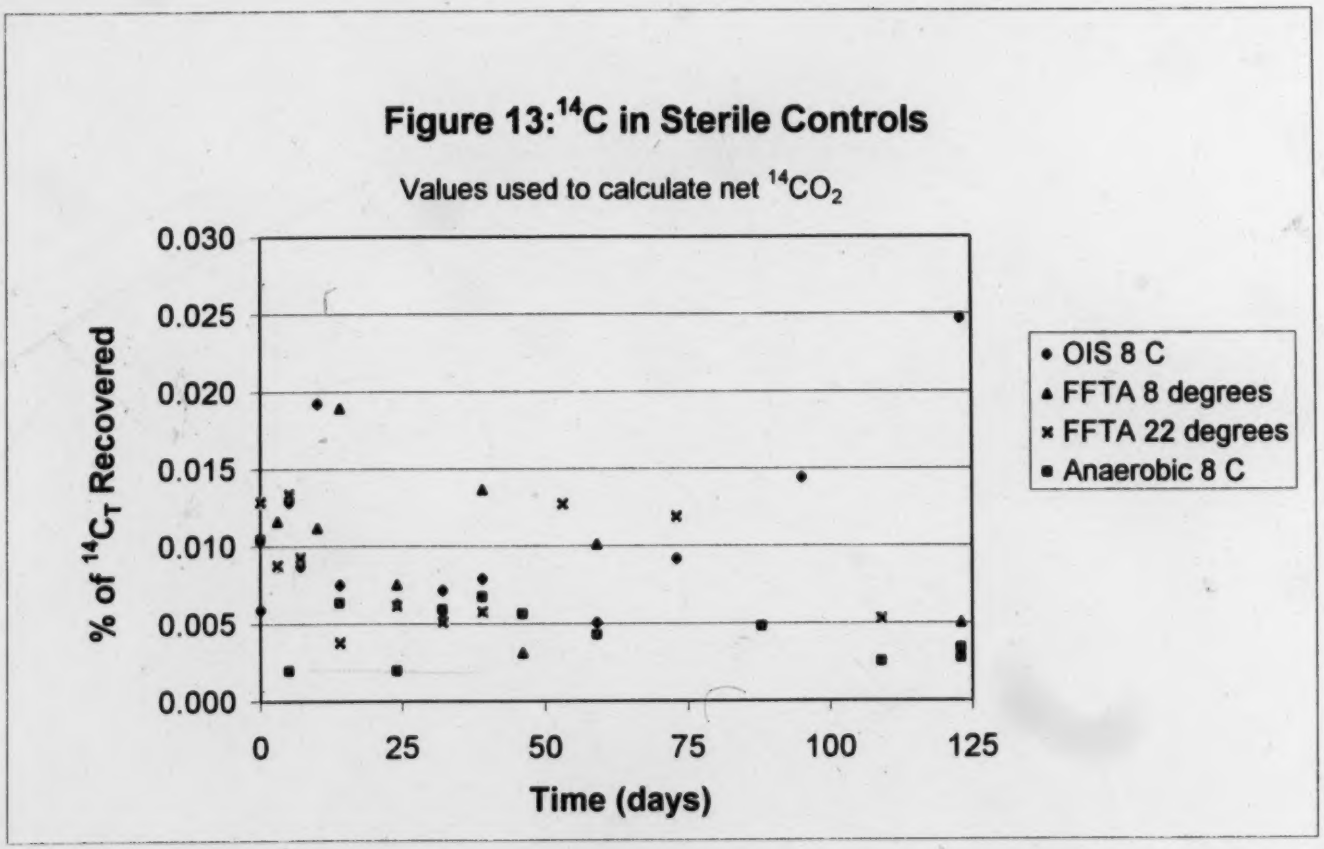
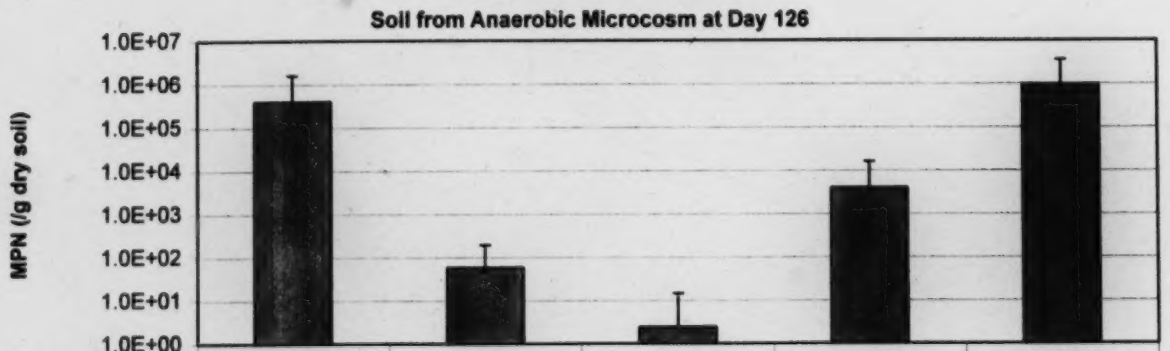


Figure 13: ^{14}C in Sterile Controls
Values used to calculate net $^{14}CO_2$
% of $^{14}C_T$ Recovered
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
25
50
75
100
125
Time (days)
OIS 8 C
FFTA 8 degrees
FFTA 22 degrees
Anaerobic 8 C

Figure 14: Anaerobic Microbial Enumeration

FFTA Microcosm Sample



	NRB >N2 gas	FeRB	SRB	JP-4	Total Het
Microcosm	4.0E+05	5.8E+01	2.4E+00	4.0E+03	9.6E+05

Error bars at 95% Confidence Interval

NRB>N2 gas = Nitrate reducing bacteria that converted nitrate to nitrogen gas
FeRB = Iron reducing bacteria
SRB = Sulfate reducing bacteria
JP-4 = JP-4 degrading bacteria
Total Het = Total Heterotrophic bacteria

Figure 15: First Order Biodegradation Rate
FFTA

Sample Conditions: Aerobic 8^{0}C

Assume 68% Conversion to $^{14}CO_2$

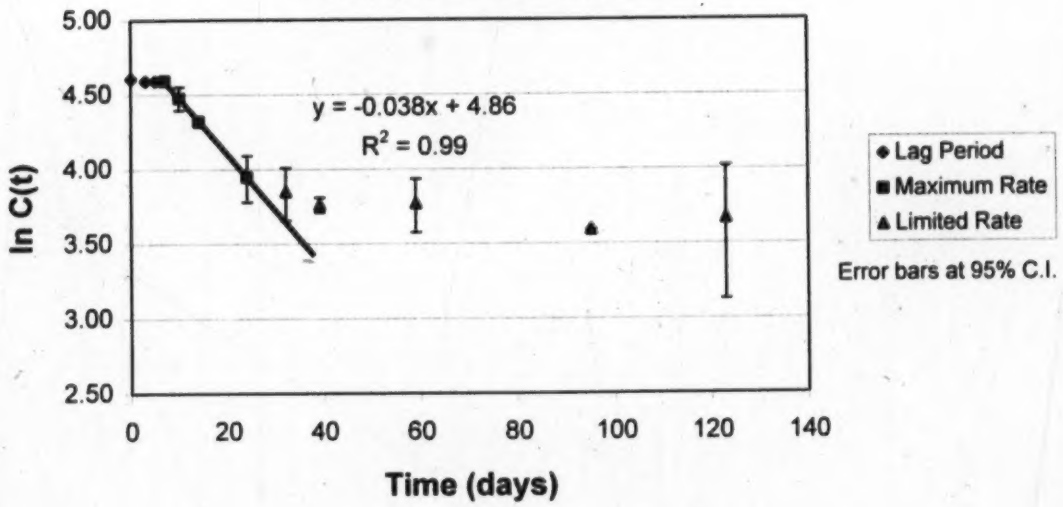


Figure 16: First Order Biodegradation Rate
FFTA

Sample Conditions: Aerobic 22°C

Assume 68% Conversion to $^{14}CO_2$

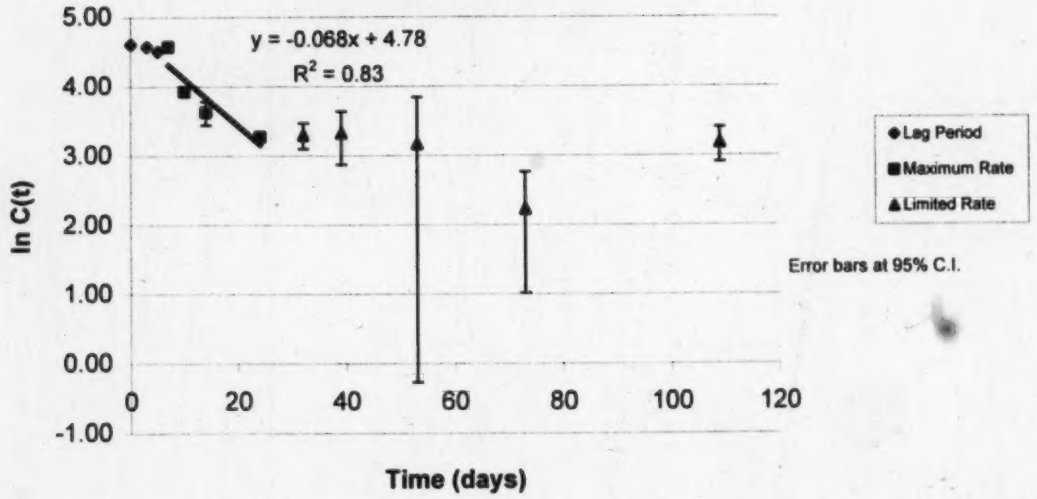


Figure 17: First Order Biodegradation Rate
FFTA

Sample Conditions: Anaerobic 8^{0}C

Assume 68% Conversion to $^{14}CO_2$

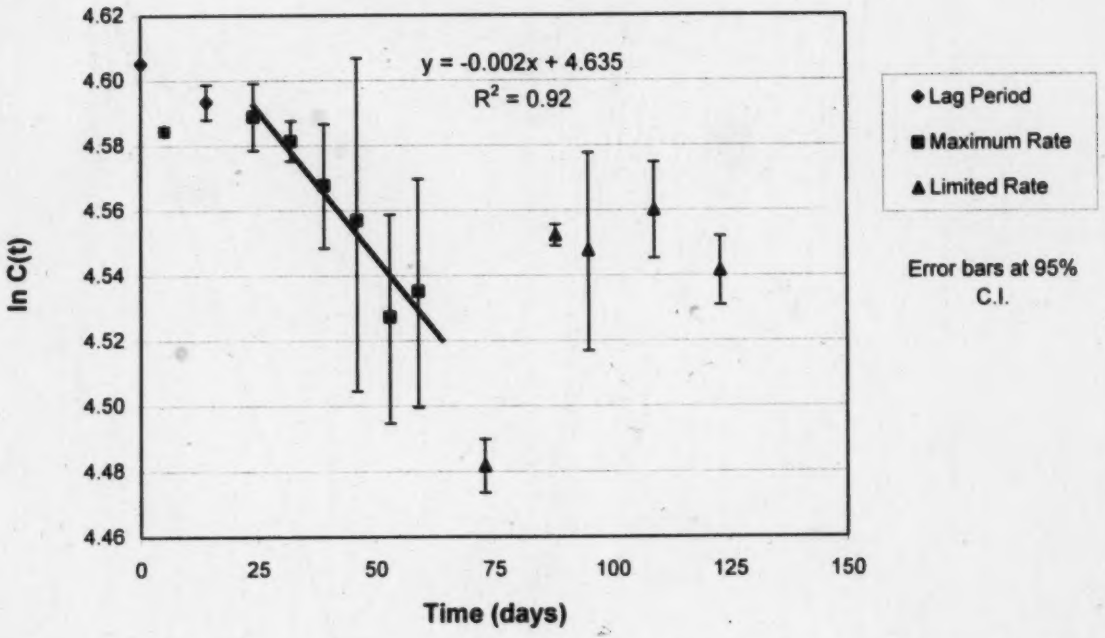


Figure 18: Declining Growth Model
FFTA 8 C

$C(t) = C_{max}(1-e^{-kt})$

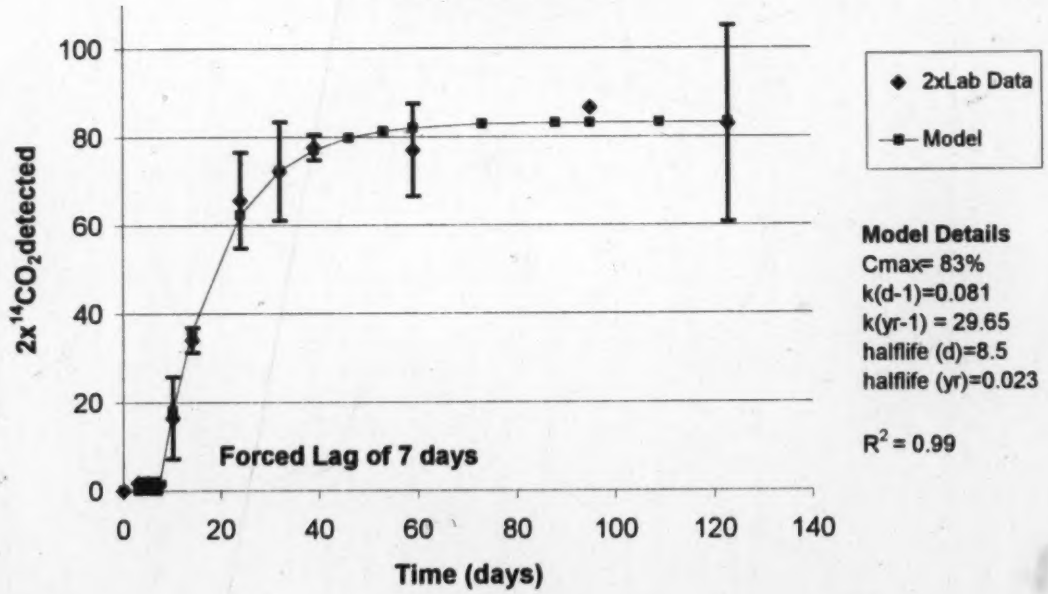


Figure 19: Declining Growth Model
FFTA 22 C

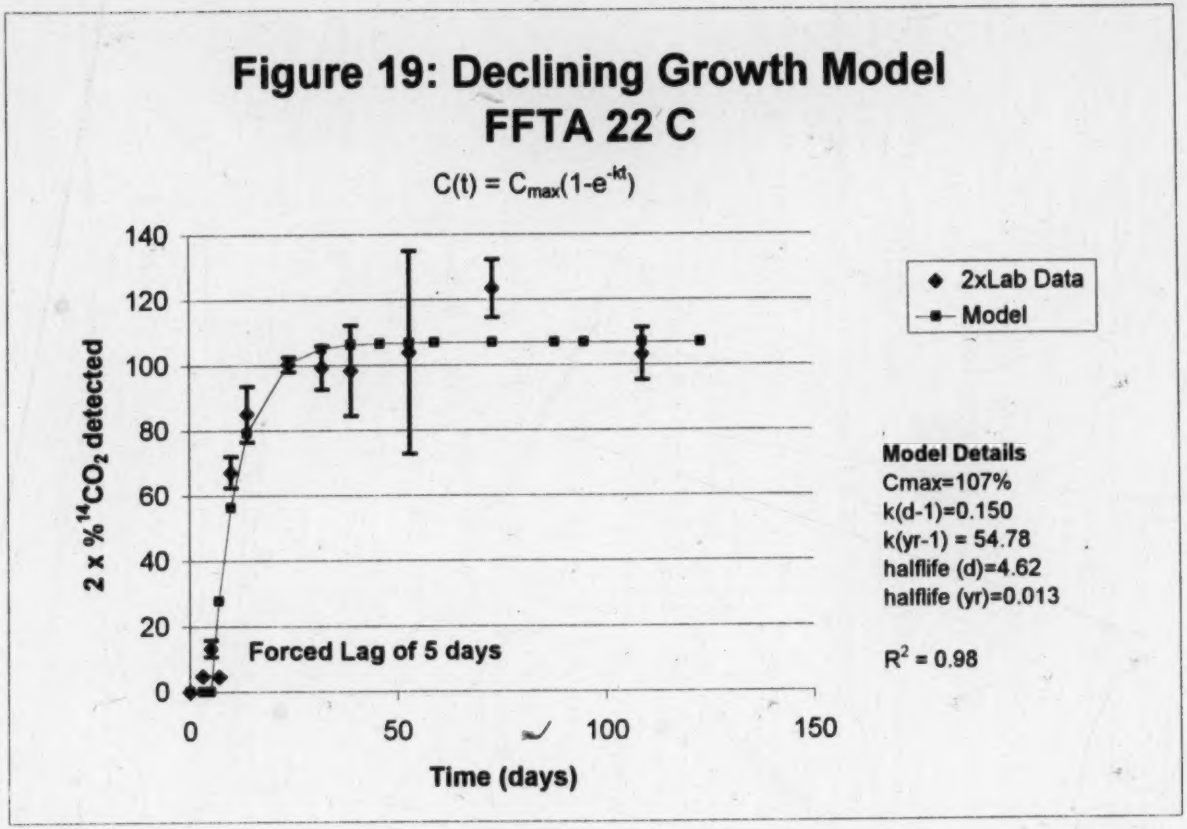
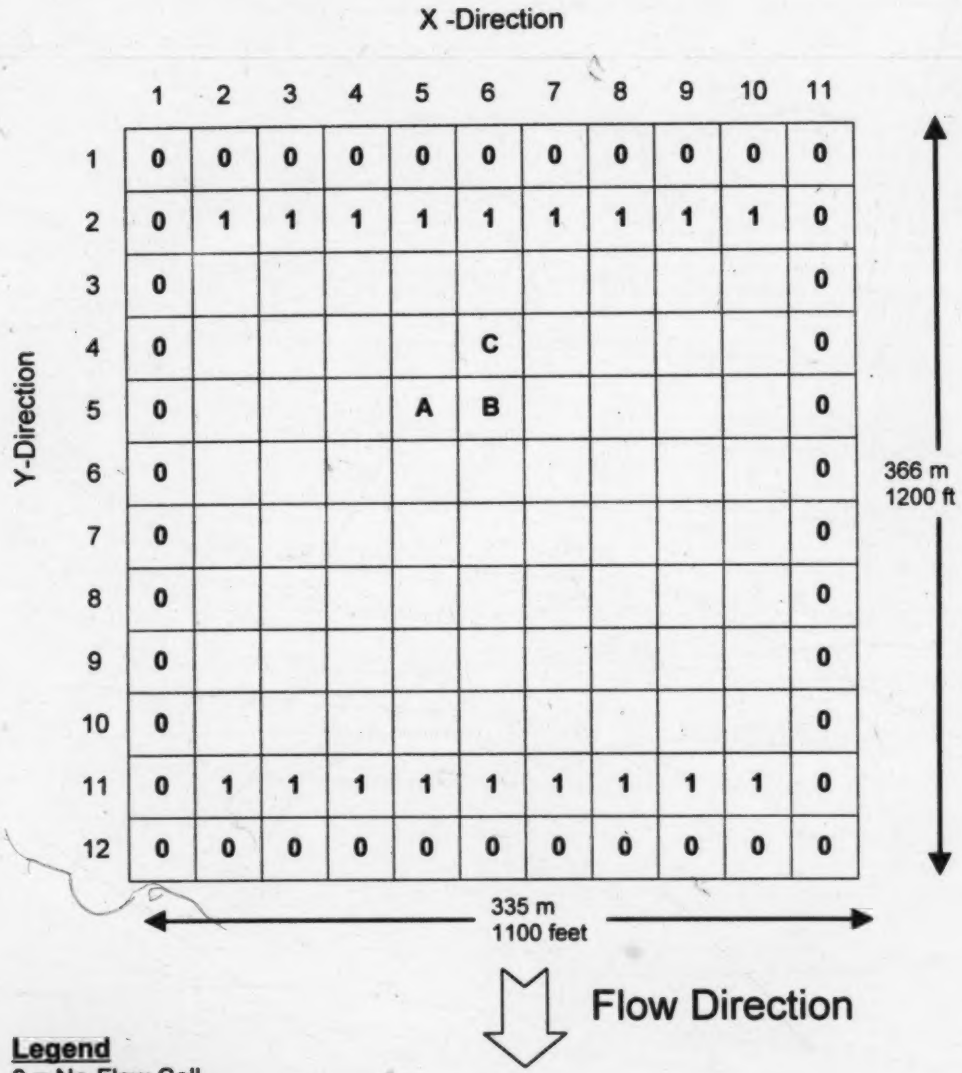


FIGURE 20

BIOPLUME II : Model Grid Characteristics



Legend

0 = No-Flow Cell
1 = Constant Head Cell
A = Source cell: Injecting 2 (10^{-4}) c.f.s. at 60 mg/L
B = Source cell: Injecting 5 (10^{-4}) c.f.s. at 220 mg/L
C = Source cell: Injecting 1 (10^{-4}) c.f.s. at 424 mg/L

Figure 21: Calibrated Model Hydraulic Head Contours

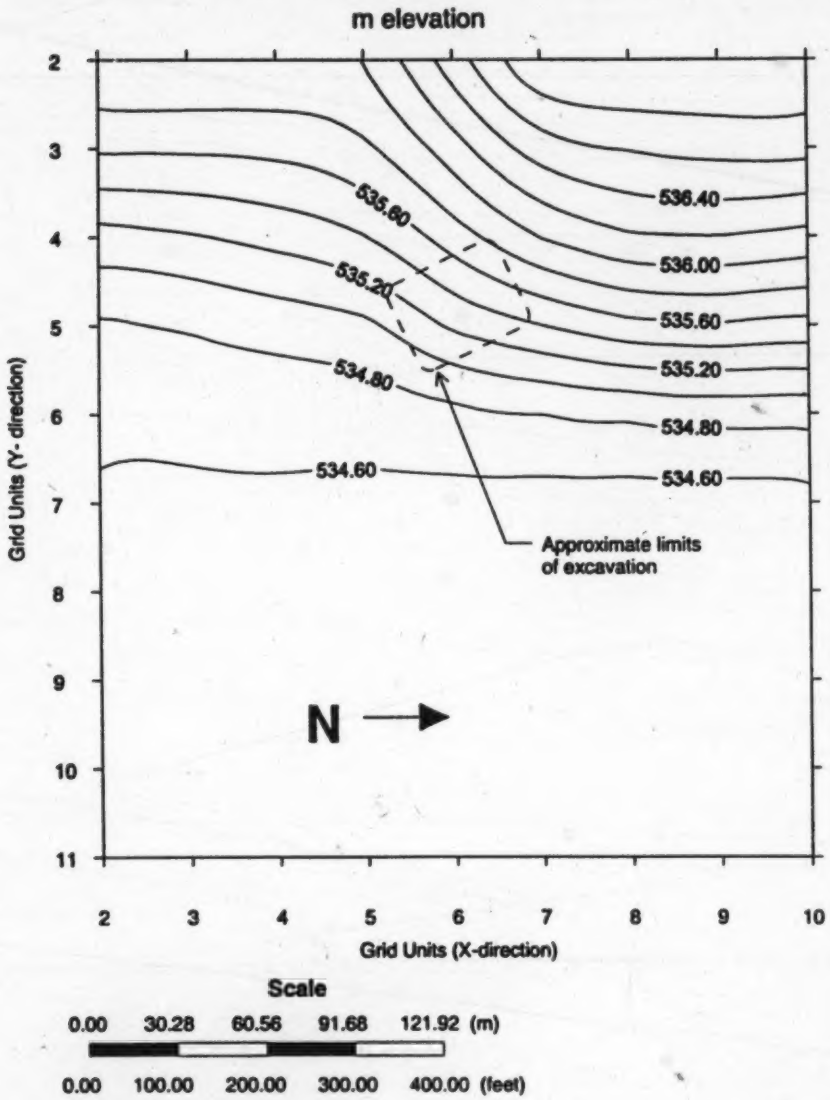


FIGURE 22: BIOPLUME II FLOW MODEL

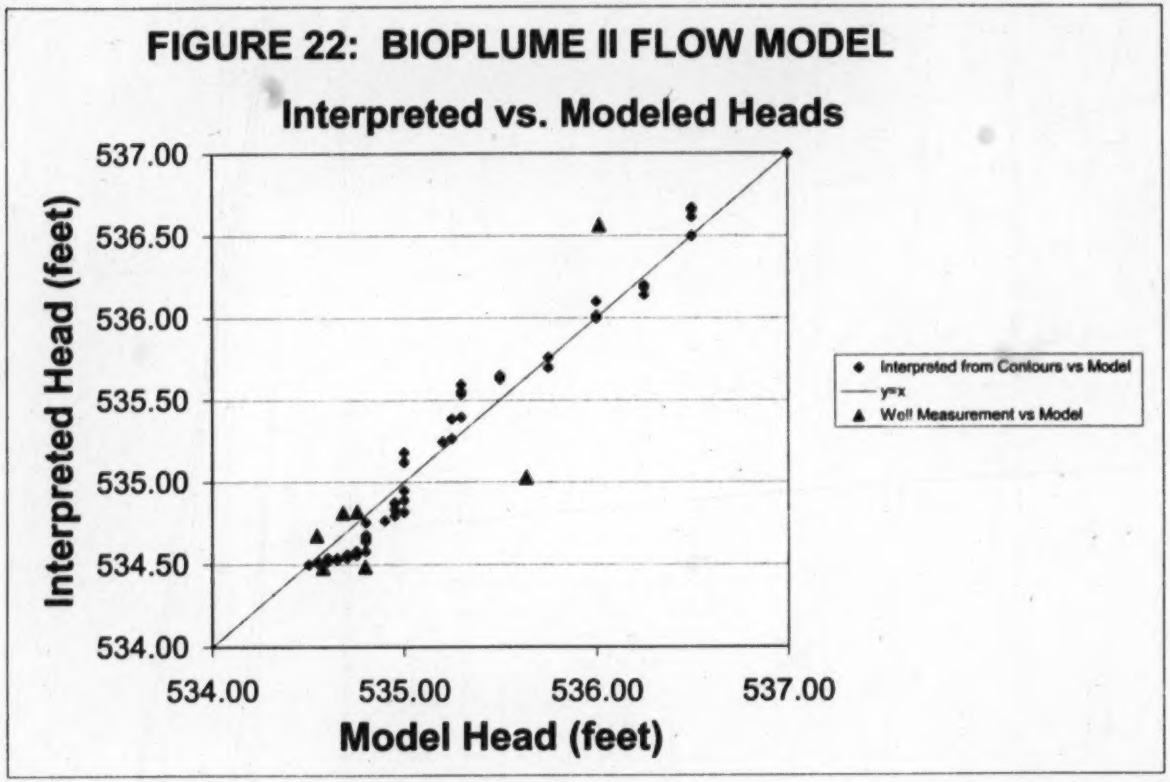


Figure 23: Calibrated Model Contaminant Contours
(overlaid on model hydraulic head contours)

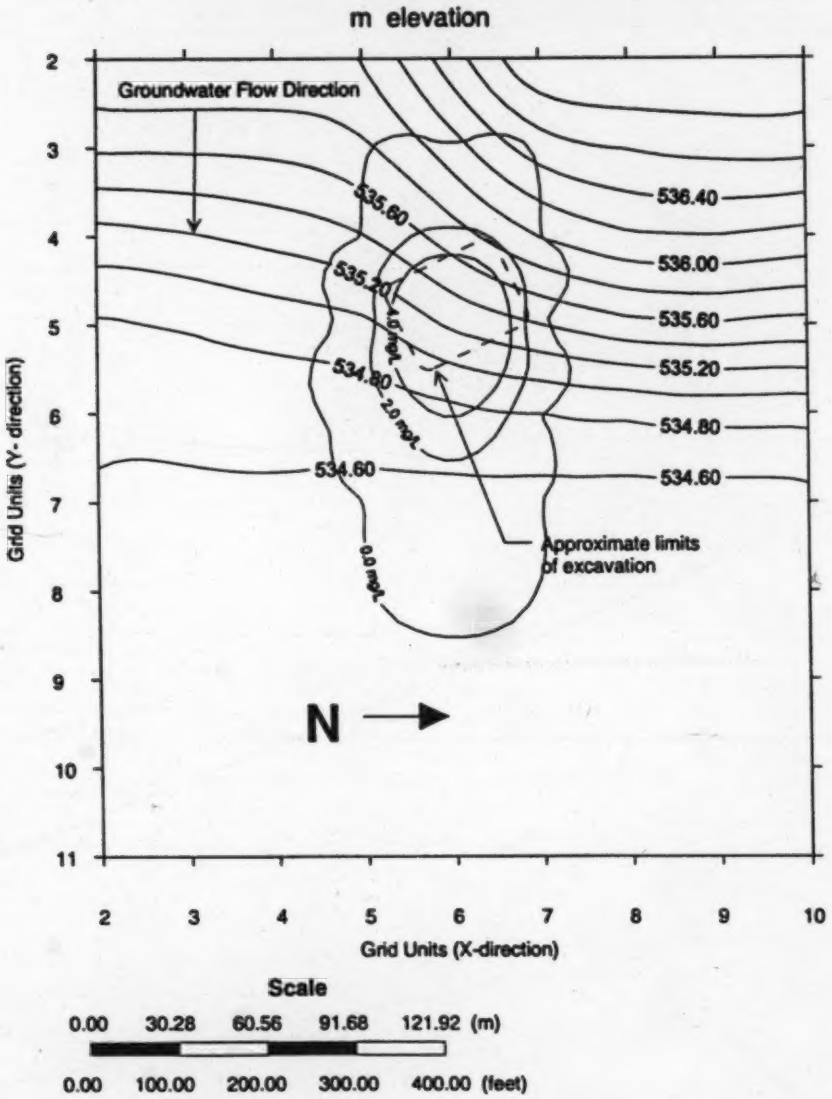


Figure 24: Calibrated Model Dissolved Oxygen Contours

Current Conditions (simulation time = 40 years)

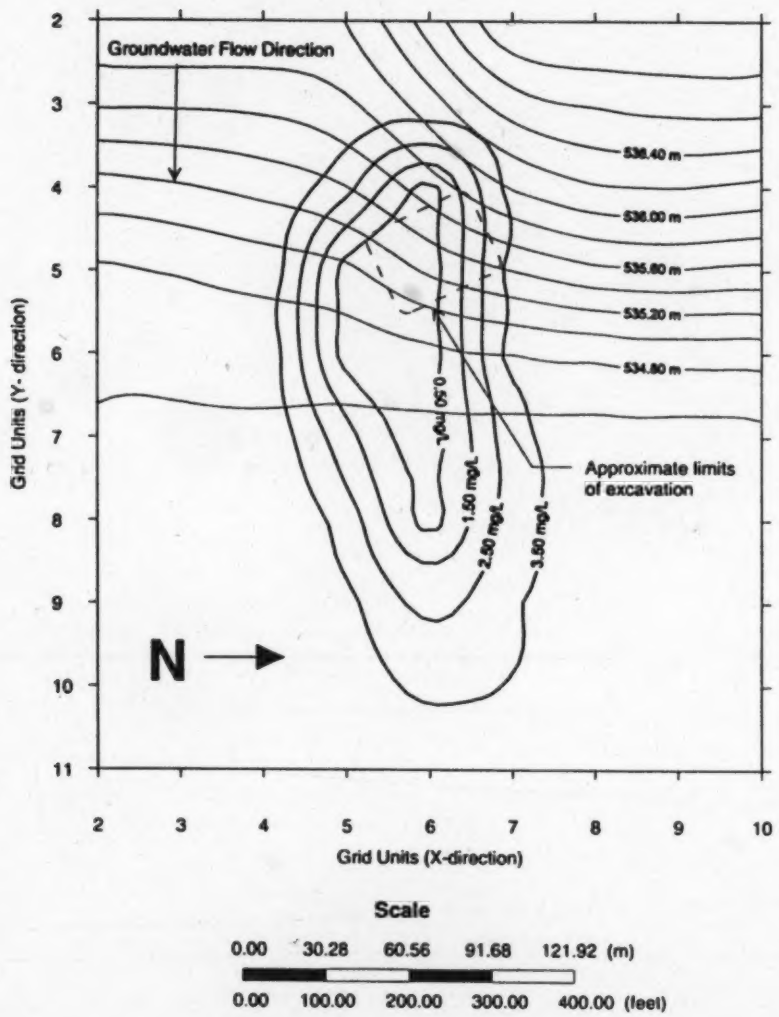


Figure 25: Calibrated Model Sensitivity Analysis

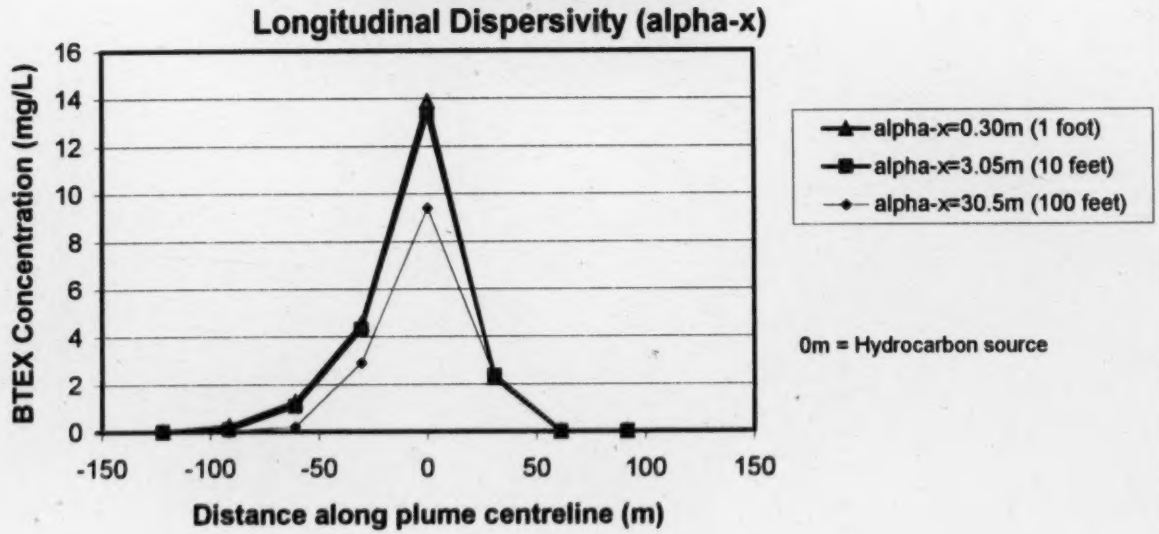


Figure 26: Calibrated Model Sensitivity Analysis

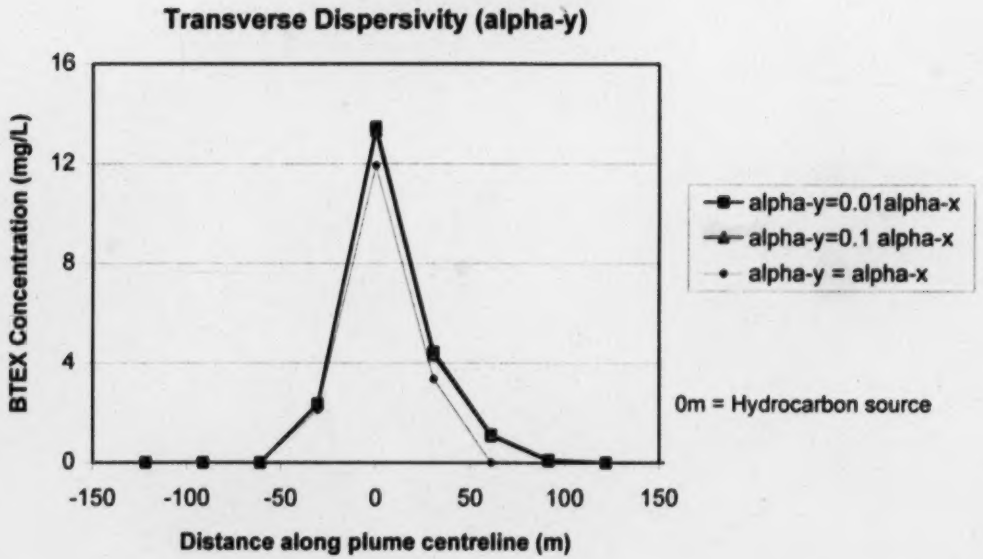


Figure 27: Calibrated Model Sensitivity Analysis

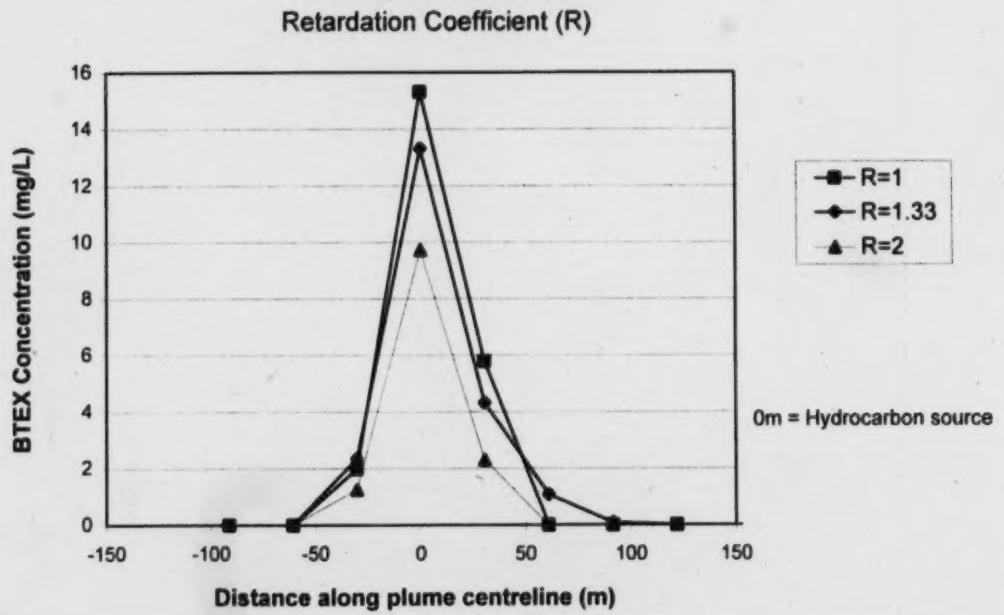


Figure 28: Calibrated Model Sensitivity Analysis
Biodegradation Parameters

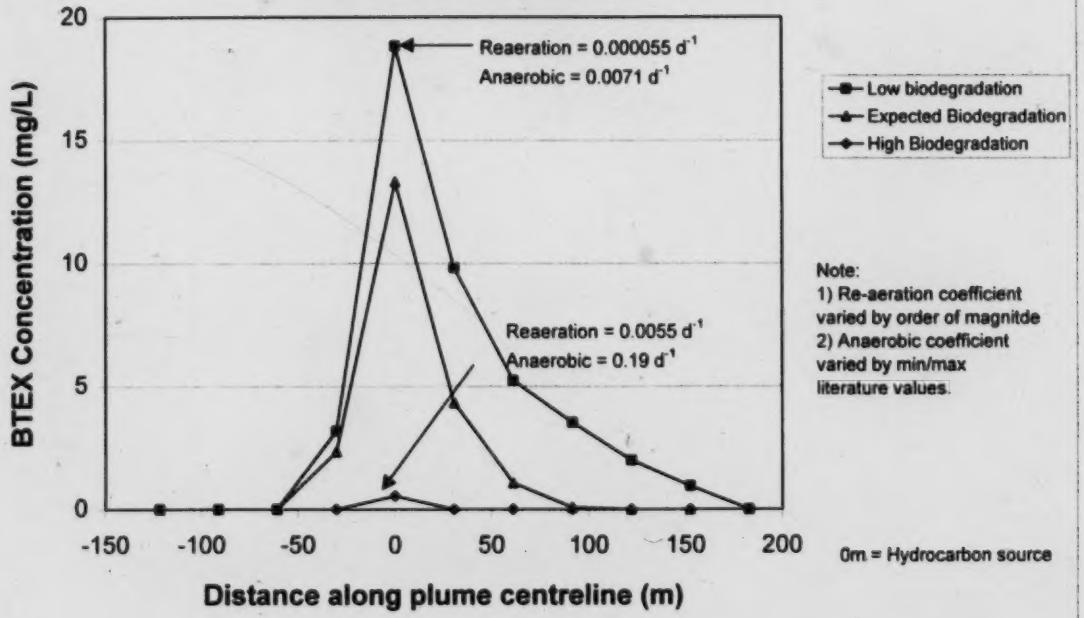


Figure 29: Calibrated Model Sensitivity Analysis

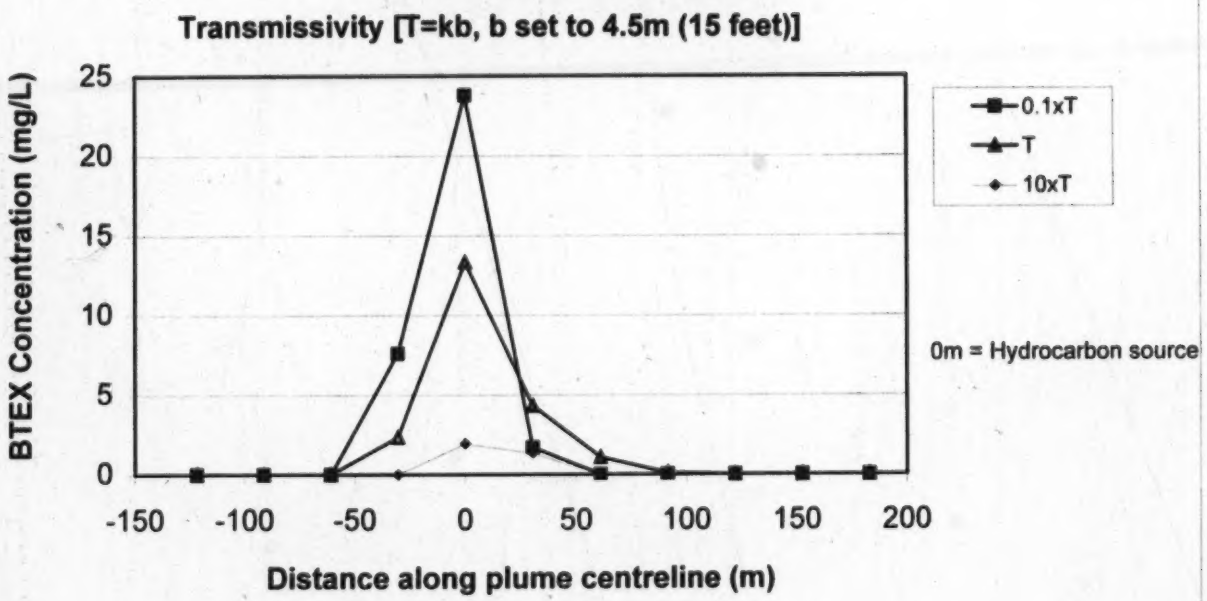


Figure 30: Calibrated Model Sensitivity Analysis

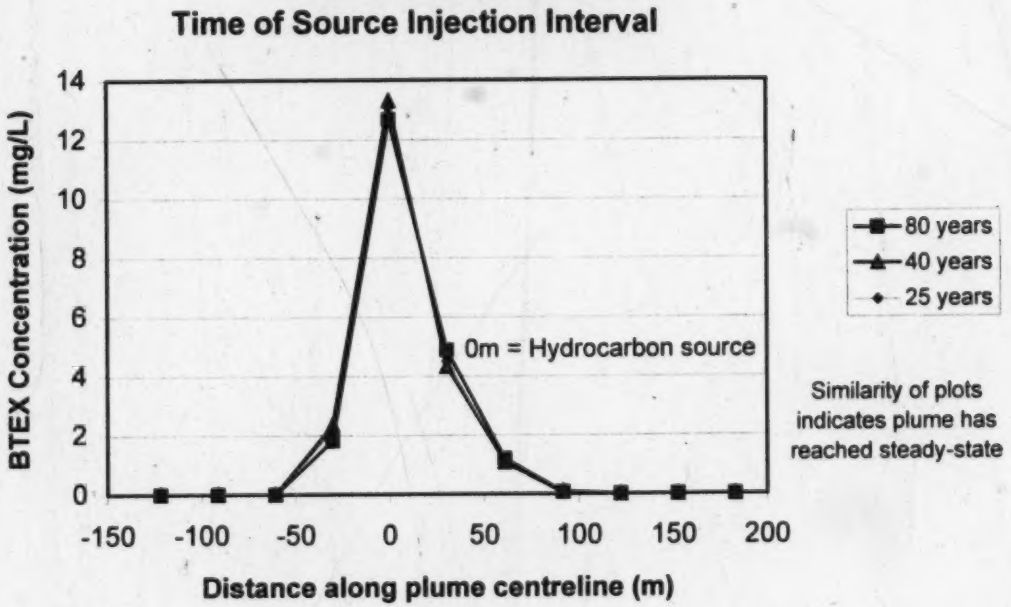


Figure 31: Model Prediction

Dissolved Hydrocarbon Concentration
When Contaminant Source Completely Removed

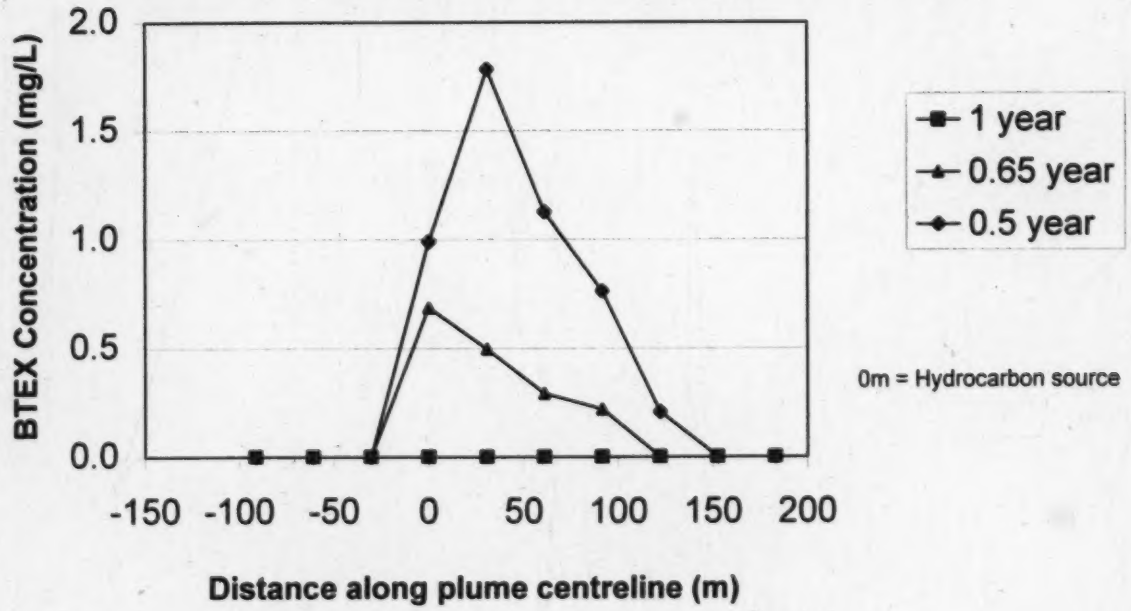
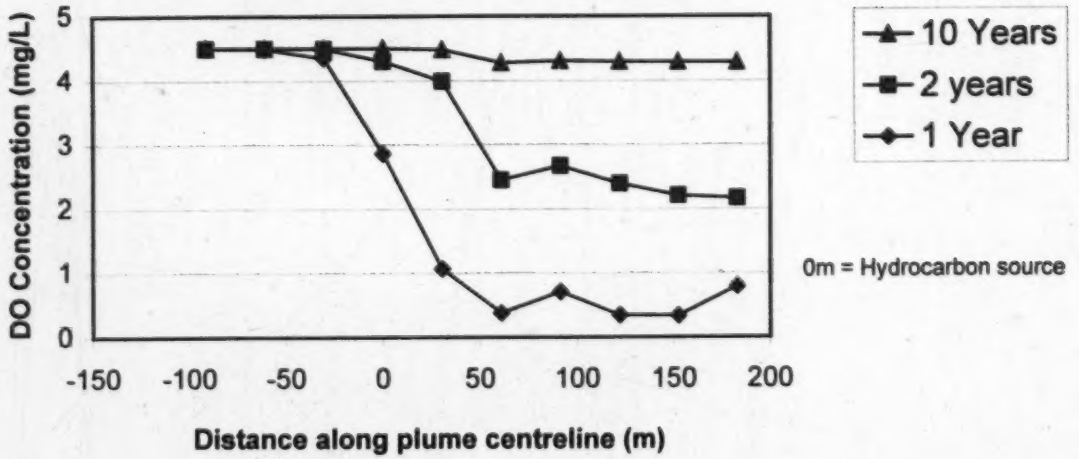
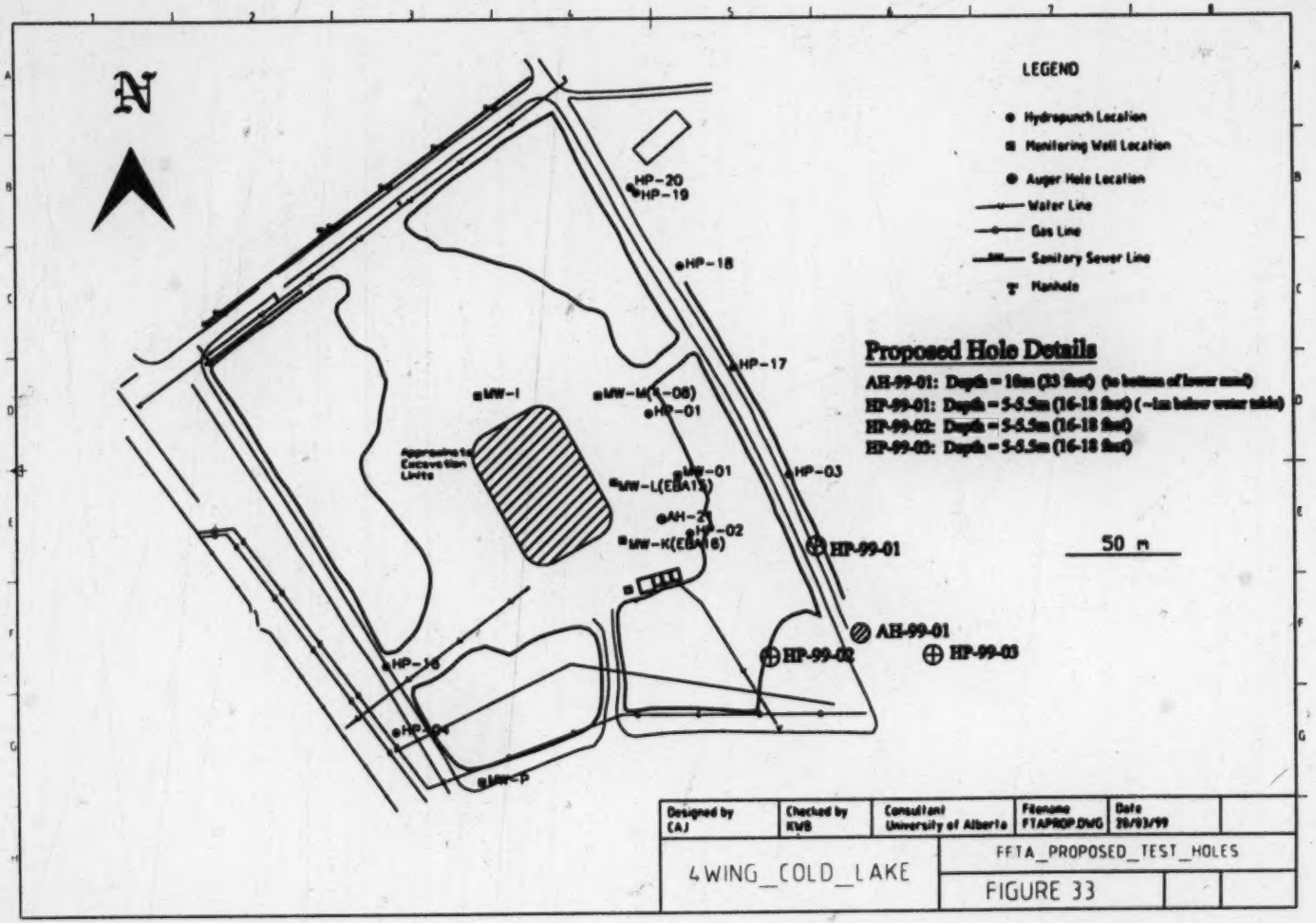
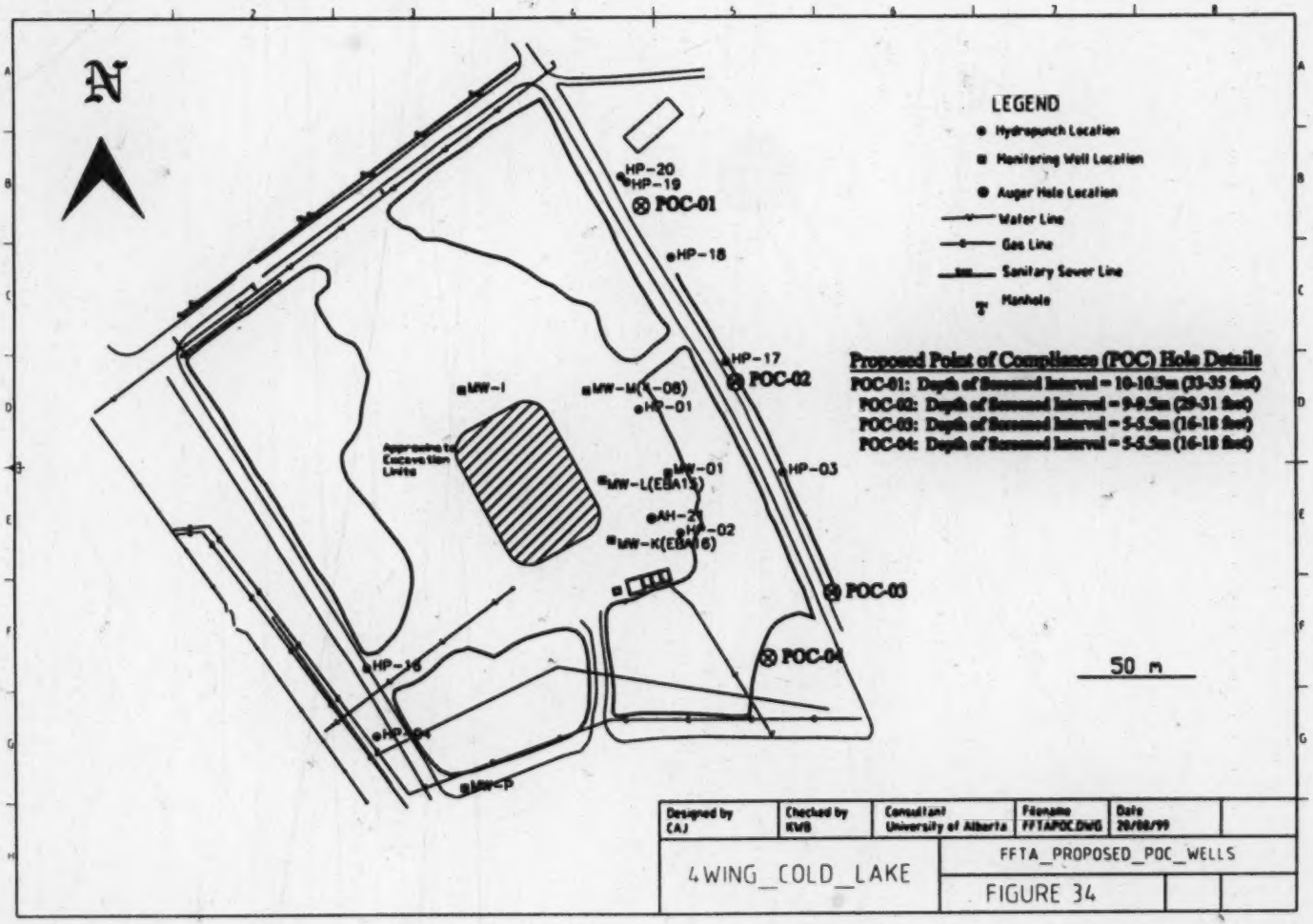


Figure 32: Model Prediction

Dissolved Oxygen Concentration
When Contaminant Source Completely Removed




N
LEGEND
Hydropunch Location
Monitoring Well Location
Auger Hole Location
Water Line
Gas Line
Sanitary Sewer Line
Manhole
Proposed Hole Details
AH-99-01: Depth = 10m (33 feet) (to bottom of lower sand)
HP-99-01: Depth = 5-6.5m (16-18 feet) (~1m below water table)
HP-99-02: Depth = 5-6.5m (16-18 feet)
HP-99-03: Depth = 5-6.5m (16-18 feet)
50 m
HP-20
HP-19
HP-18
HP-17
HP-03
HP-01
HP-02
MW-I
MW-L(EBA12)
MW-K(EBA16)
MW-01
AH-21
HP-99-01
AH-99-01
HP-99-02
HP-99-03
Designed by (AJ)
Checked by KWB
Consultant University of Alberta
Filename FTAPROP.DWG
Date 28/03/99
4WING_COLD_LAKE
FFTA_PROPOSED_TEST_HOLES
FIGURE 33


N
LEGEND
Hydropunch Location
Monitoring Well Location
Auger Hole Location
Water Line
Gas Line
Sanitary Sewer Line
Manhole
Proposed Point of Compliance (POC) Hole Details
POC-01: Depth of Screened Interval = 10-10.5m (33-35 feet)
POC-02: Depth of Screened Interval = 9-9.5m (29-31 feet)
POC-03: Depth of Screened Interval = 5-5.5m (16-18 feet)
POC-04: Depth of Screened Interval = 5-5.5m (16-18 feet)
HP-20
HP-19
POC-01
HP-18
HP-17
POC-02
MW-I
MW-M(98-08)
HP-01
MW-01
HP-03
MW-L(ESA15)
AH-21
HP-02
MW-K(ESA16)
POC-03
POC-04
HP-16
MW-P
50 m
Designed by CAJ
Checked by KWB
Consultant University of Alberta
Filename FFTAPOC.DWG
Date 20/08/99
4WING_COLD_LAKE
FFTA_PROPOSED_POC_WELLS
FIGURE 34

5 OLD IMPERIAL SITE

A study was conducted at a second site; an abandoned gas station located at the southwest corner of Kingsway Road and Hangar Lane at 4 Wing Cold Lake. The station operated for approximately 25 years and was demolished between 1979-1981. Figure 35 shows the current layout of the site and Figure 36 shows the original Imperial Oil gas station layout (Environment Canada - Federal Programs Division, 1995). Contamination of the soil and groundwater likely resulted from both surface infiltration of spillage and from leaking underground petroleum storage tanks. Numerous investigations to delineate the contaminant plume have been carried out by a number of different consultants.

5.1 Scope of Work

The investigation at this site sought to resolve the location of the contaminant plume and investigate the potential for intrinsic bioremediation of the contaminants of concern. The relatively low gradient across the site combined with the dominantly low permeability clay suggested that the mobilization of contaminants of concern off the site was low-risk. This site has likely contained subsurface contamination for many years and significant levels have not been detected off site more than 40m in the downgradient direction.

5.2 Previous Studies

At least six separate site investigations have been carried out since subsurface hydrocarbon contamination was suspected in 1991. These investigations reported on augered test holes, groundwater monitoring well installations, geophysical testing, and soil, vapour and groundwater sampling and analysis.

In August 1991, Custom Environmental Services reported on BTEX contamination present in soil and water sampled from an excavation at the corner of Kingsway Road and Hangar Lane (likely dug to access underground utilities at this location) and also from shallow auger holes drilled north and east of the intersection. Follow-up investigation in October 1991

involved 12 test holes (including six monitoring well installations), and interpretation of groundwater flow to the north-northwest (see Figure 37). Trace levels of hydrocarbon contamination were reported from soil samples to the north of Kingsway road, but no analytical testing of soil or groundwater from the former gas station property was carried out (Custom Environmental Services, 1991).

An electromagnetic geophysical survey carried out by Geo-Physi-Con in September 1991 was not able to delineate hydrocarbon contamination, but did locate two conductive anomalies suggesting buried metal objects. One of these anomalies correlates to the location of the previous retail gasoline storage tank that was removed during the gas station demolition (Figure 36). This survey indicates that segments of the original installation may remain in the ground. The conductivity contour maps for the EM 31 survey are included as Figures 38 and 39 (Geo-Physi-Con Ltd., 1991).

HBT Agra reported on five monitoring wells installed in late 1993 that intercepted hydrocarbon contamination (see Figure 40). Elevated levels of hydrocarbon gas vapour in the soil (700-4200ppm) were detected in two test holes (167.1A, 167.2) to depths of 4.0m below ground. Two soil samples were analyzed from 167.1A, one at 3.0m depth and another at 6.7m depth. The sample at 3.0m contained 1.6, 6.1, 3.7, and 17 mg/kg [ppm] BTEX compounds respectively, and 230 and 234.7 mg/kg [ppm] TVH and TPH respectively. The sample at 6.7m exhibited non-detectable BTEX concentrations and trace levels of Total Volatile Hydrocarbons (TVH) and Total Petroleum Hydrocarbon (TPH). Phenol, a degradation product of benzene, was also detected at 0.2 mg/kg [ppm] in the shallow soil sample and trace levels of lead were measured in both samples. Groundwater sampled from monitoring wells at 167.1B (2.0-3.7m screen interval) and 167.2 (0.3-3.3m screen interval) exhibited 33 and 110 mg/L [ppm] TPH levels, respectively. Groundwater sampled from the monitoring well installed at 167.1A (1? -6.5m screen interval) contained non-detectable levels of BTEX. The test hole advanced on the north side of Kingsway road (TH 205) exhibited soil hydrocarbon vapours at less than 150 ppm, and contained no detectable BTEX in a soil sample. The groundwater sampled from the monitoring

well installed at that location contained 2 ppb benzene and no detectable toluene, ethylbenzene or xylenes (AGRA Earth & Environmental Group, 1994).

A November 1994 excavation to install a water line across the site parallel to Kingsway road initiated a trench fire that precipitated further contaminant investigations. An Environment Canada report dated January 1995 contains a 1978 plan map (Figure 36) showing the approximate location of the former Imperial Oil facilities, including the 22730 litre underground steel fuel tank and the pump islands (Environment Canada - Federal Programs Division, 1995).

Agra Earth and Environmental submitted a Phase II Environmental Site Assessment in September 1997. Eleven auger holes were drilled with four monitoring wells installed at the site (see Figure 41). High soil hydrocarbon vapour levels were measured in six test holes with peak levels at 2.0-4.5m depth below ground. Four soil samples were analyzed for BTEX and TPH contamination with results as summarized in the table below.

Soil Analytical Results (AGRA Earth & Environmental, 1997)

Sample Location	Benzene (ug/g)	Toluene (ug/g)	Ethylbenzene (ug/g)	Xylenes (ug/g)	TPH (ug/g)
97-2 @ 6.0m	0.006	<0.005	<0.005	<0.005	NA*
97-3 @ 3.8m	4.1	9.2	4.6	14	230
97-4 @ 2.3m	0.074	0.35	<0.005	<0.005	NA*
97-6 @ 3.1m	19	64	39	180	820

*NA: not analyzed

Significant levels of dissolved BTEX contamination in the groundwater were also detected in monitoring wells 97-3 and 97-6 as summarized in the table below.

Groundwater Analytical Results (AGRA Earth & Environmental, 1997)

Monitoring Well	Benzene (mg/L)	Toluene (mg/L)	Ethylbenzene (mg/L)	Xylenes (mg/L)
97-1	<0.001	<0.001	<0.001	<0.001
97-2	<0.001	<0.001	<0.001	<0.001
97-3	4.0	1.6	0.02	3.0
97-6	6.2	6.6	3.9	17

Recommendations in the report included two follow-up test holes to be located downgradient to investigate the possibility of off-site migration of contaminants (AGRA Earth & Environmental, 1997). One well has since been installed at the southeast corner of Kingsway road and Hanger lane (MW-H, Figure 35) but the NW corner could not be drilled due to the presence of underground water and sewer lines (AGRA Earth and Environmental, 1998).

Review of the information in these reports provided an understanding of the site history, subsurface stratigraphy and groundwater flow direction, and an indication of the extent of soil and groundwater contamination at the time of the studies.

5.3 Investigation Methodology

A significant amount of subsurface investigation had been carried out prior to this investigation providing an extensive preliminary site characterization. The presence of a number of monitoring wells provided access to groundwater samples, which were analyzed to indicate the concentrations of contaminants and TEAs upgradient, near the source area, and downgradient. Additional hollow stem auger holes with continuous split-spoon sampling permitted a careful search for conductive layers within the contaminated region, and the installation of a monitoring well within the plume was required for hydrogeological testing. HydroPunch® holes were not attempted due to the likelihood of the low permeability clay preventing adequate flow for groundwater sampling. Enumeration of soil microbes and a batch-type microcosm study were carried out to characterize the microbial community and confirm the potential for biodegradation. Because the ground temperatures at 4 Wing are considerably colder than those sites where intrinsic bioremediation has been documented in the literature, the laboratory tests were performed at the average *in situ* temperature (8°C).

This section of the report only describes the work performed in the field. The results of the analysis of samples taken, or tests conducted in the field are discussed in detail in subsequent sections.

5.3.1 Sampling Program

Field investigations were initiated on three separate occasions. Initial site reconnaissance and groundwater sampling of selected existing monitoring wells was carried out in June 1998. Groundwater table elevations were measured and the presence of free product or hydrocarbon odour was recorded for all remaining wells. In August 1998, an auger drill rig equipped with both solid stem and hollow stem augers was brought on site and eight test holes were advanced. One monitoring well was installed and selected existing monitoring wells were

sampled for contamination and geochemistry. A site visit in October 1998 permitted a final round of water table elevations to be recorded, a soil sample for laboratory biodegradation microcosm analysis to be obtained, and hydrogeological testing to be carried out.

The site was sampled in sequence from areas of least contamination towards the suspected source area. Quality assurance techniques were applied through the use of rinsate blanks and duplicate groundwater samples. Figure 35 shows the locations of the samples taken during this study. Soil and groundwater samples were taken upgradient, within the contaminated source area, and downgradient to delineate contamination, to examine TEA utilization, and to conduct laboratory microbial analysis.

5.3.1.1 Soil Vapour Sampling Method

Elevated carbon dioxide (CO_2) levels in the soil are an indication of bioactivity and thus indirect evidence for hydrocarbon biodegradation. Lower explosive limit (LEL) levels provide an indication of the extent of hydrocarbon contamination in a soil sample. Selected soil samples were retrieved from the split-spoon or auger flights and placed in a plastic sampling bag. Readings were taken with a gas detector by inserting a sampling tube into the bag after equilibrium conditions were reached (5-10 minutes).

5.3.1.2 Soil Sampling Method

Soil samples were obtained using a hollow stem auger and an unlined 8.6cm (3-3/8") diameter split-spoon sampler. The continuous hollow stem coring of the soil reduced sample disturbance and thus permitted both better delineation of stratigraphy and better soil sample quality for chemical analyses than solid stem coring could provide. The cores were inspected and described according to the Unified Soil Classification System (Borehole logs are included as Appendix A). For chemical analysis, subsamples of intact clumps of soil were placed into 250mL glass jars and immediately sealed with Teflon®-lined lids and minimal headspace.

All sampling equipment was rinsed with methanol and de-ionized water between sampling intervals. Potentially contaminated drilling equipment was cleaned with high-pressure

steam between boreholes. Soil samples for chemical analysis were stored no longer than 10 days, in the dark, and at approximately 4°C until analyzed at ETL, Edmonton.

5.3.1.3 Groundwater Sampling Method

Groundwater samples were analyzed for the presence of hydrocarbons (each component of BTEX, volatile and extractable hydrocarbons), terminal electron acceptors (dissolved oxygen (DO), nitrate, nitrite, sulfate), biodegradation by-products (sulfide, methane and soluble iron), pH, electrical conductivity, redox potential, and temperature.

The techniques employed to obtain and preserve groundwater samples are identical to those at the FFTA as described in Section 4.3.1.3. The pump was disassembled, cleaned and rinsed with distilled water after every well was sampled. Periodically after cleaning, distilled water was flushed through the entire pump system and sampled to confirm that it was not contaminated.

In wells where free product was indicated at the water surface or where the water column in the well was too small, a disposable low-flow bailer was employed to fill sample containers with minimal disturbance and no headspace. Water was gently poured down the side of sample vials so as not to agitate or create bubbles, which could strip gases dissolved in the water. Samples were immediately incubated at approximately 4°C in coolers.

5.3.1.4 Soil and Groundwater Sample Analysis

Analysis for hydrocarbons, nitrate, nitrite, sulfate, sulfide and iron (II) were carried out at ETL, Edmonton. A detailed account of the analytical methods employed by ETL for all chemical analyses is included as Appendix E. Methane analysis was performed at the University of Alberta by headspace gas chromatographic technique with a flame ionization detector as described in Section 4.3.1.4. Field measurements of pH, electrical conductivity, dissolved oxygen, redox potential and temperature were obtained by calibrated hand-held meters in a flow-through cell.

5.3.2 Field Hydrogeological Testing

During each of the three field visits, measurement of the groundwater table elevation in selected monitoring wells was carried out. These measurements allowed determination of the direction of groundwater flow and the gradient across the site. Permeability testing of three monitoring wells was attempted.

5.3.2.1 Groundwater Table Investigations

Groundwater elevations were measured at approximately 16 monitoring wells across the site on three occasions (June, August, and October 1998). This information, along with the monitoring well details is summarized in Table 10. In addition, a total station survey was performed to accurately determine the location of the wells and test holes.

5.3.2.2 Permeability Tests

Slug testing provides an efficient means of estimating the hydraulic conductivity in the ground immediately around a borehole. A solid PVC slug was used to displace water in selected wells while monitoring the change in head as described in Section 4.3.2. Unfortunately, the response of the water level within the monitoring wells tested was either too fast or too slow, preventing meaningful interpretation. The hydraulic conductivity was therefore estimated based on the geologic materials at the site.

5.4 Geological Analysis

The character of the sediment and the geologic stratigraphy can control the rate and extent of contaminant migration. The soil moisture content (w) and fraction organic carbon (f_{OC}) were characterized by laboratory analysis of samples gathered at the site. The geologic setting was interpreted by combining information from previous subsurface investigations with the borehole logs for this investigation (Appendix A).

5.4.1 Laboratory Characterization: Moisture Content and Fraction Organic Carbon

Analysis of moisture content (w) was carried out on five samples from below the water table in auger holes spread over the site. Tests were carried out in triplicate following the method recommended by the ASTM D2216-80. Results indicate that the average moisture content of the soil sampled was 19 ± 3%.

The fraction organic carbon (f_{OC}) is the mass ratio of organic carbon to soil, and was determined to average 2.1 ± 0.5% for two samples obtained from AH-12 and AH-15. The method used is described by ASTM D2974-87. Tests were carried out in triplicate and the muffle furnace temperature set to 440°C to burn off soil organic material. The data collected for the calculation of the moisture content and fraction organic carbon are included as Appendix B.

5.4.2 Geologic Profile

Test holes to investigate subsurface stratigraphy at the site reveal a very thin layer of topsoil overlying at least 5m of mottled, weakly oxidized stiff silty sandy clay till with trace cobbles and rare iron-stained fractures. At one location, a gravelly sand fill material up to 3.0m thick was encountered near the surface (167-3). A 0.15-0.20m thick, discontinuous sandy gravel layer appears at approximately 3m depth in some test holes (incl. AH-14 and AH-15). These findings do not bear out the presence of a 1.5m thick sand layer at 3-4m depth that was indicated by a previous investigation at MW-97-6 (AGRA Earth & Environmental, 1997). Further delineation of the thickness and extent of this layer is critical to an understanding of contaminant migration at the site. Fresh, unfractured dark greenish-grey till is present below 5m. A number of underground utilities are buried at the site, including both drinking water lines and sewer lines (Figure 35). These utilities are commonly buried with a sand bedding and may have a sand and gravel fill, which complicates interpretation of the local groundwater flow regime as some utilities appear to act as conduits for groundwater and contaminant migration.

5.5 Hydrogeological Analysis

Field measurements of water table elevation were plotted to assess the gradient across the site on three separate occasions. When combined with an estimate of hydraulic conductivity, this information permits calculation of the groundwater velocity. An estimate of the rate of contaminant migration across the site can then be made upon consideration of the influence of adsorption.

5.5.1 Water Table Gradient

The direction of regional groundwater flow is toward a tributary of Marie Creek, approximately 150m to the north of the site. The water table is unconfined and resides in the till or fill material 1.5 - 2m below ground. It did not fluctuate significantly over the sampling period. A complete listing of groundwater elevation measurements and monitoring well details is included as Table 10. A contour plot of groundwater table elevation for each month of the sampling period is included as Figures 42-44. The direction and magnitude of the water table gradient remained approximately constant over the testing period. The gradient across the site was calculated to be approximately 0.035m/m in a northeasterly direction (calculations shown on each figure).

5.5.2 Hydraulic Conductivity

Slug tests were attempted in monitoring well 97-6, but the fast response of the water table prevented meaningful interpretation. Because the water level resided within the screened interval at the time of testing, displaced water was able to flow into the unsaturated zone, which likely offered less resistance to flow. Tests were also attempted in monitoring wells 97-3 and MW-14A, but after the introduction of the slug into these wells there was no measurable response from the water level in the well over the monitoring period. This suggests that the surrounding till had sufficiently low permeability that the displaced water could not dissipate at an easily measurable rate. An estimate of the conductivity can be made based on the geologic materials at the site. Silty clay till, which is present over most of the area, typically exhibits a permeability ranging from 10^{-6} to 10^{-9} m/s (Freeze and Cherry, 1979). The discontinuous thin gravelly sand

layers and the sand beds surrounding the utilities crossing the site have likely acted as preferential flow paths. The hydraulic conductivity in this material could reach as high as 10^{-3} m/s.

Given the heterogeneous nature of the site, the minimum, maximum and expected hydraulic conductivity of the till covering most of the site may vary by an order of magnitude, and was therefore estimated to be $1x10^{-8}$m/s, $1x10^{-6}$m/s, and $1x10^{-7}$m/s respectively.

5.5.3 Groundwater Velocity

Given the gradient (change in groundwater table elevation) across the site shown by the groundwater elevation contours, and the assumed permeabilities based on the field investigation, the expected horizontal specific discharge was calculated by Darcy's Law as described in Section 4.5 to be only 0.1m/yr. Difficulties in estimating the permeability arose due to the heterogeneous nature of the subsurface at the Old Imperial site. The flow behaviour is complex and thus a wide range of error must be considered for the sensitivity analysis.

The seepage velocity was calculated by dividing the specific discharge (ν) by the porosity (n) of the aquifer. The total porosity was calculated to be 0.33 by the technique described in Section 4.5 which relates an estimate of the soil water content (19 ± 5%) and void ratio (0.50) by Equations 7 and 8. This is slightly higher than typical values of effective porosity for clay and glacial sediments which can vary from 0.05 to 0.20 (Wiedemeier et al., 1995). A conservative estimate for effective porosity is 0.25. Maximum, minimum and expected specific discharge and seepage velocities are summarized below.

	Permeability (m/s)	Gradient (m/m)	Specific Discharge (m/yr.)	Seepage Velocity (m/yr.)
Maximum	10^{-6}	0.043	14	56
Minimum	10^{-8}	0.027	0.009	0.04
Expected	10^{-7}	0.035	0.1	0.4

5.5.4 Retarded Contaminant Migration

Retardation of dissolved contaminant migration relative to the groundwater velocity occurs when contaminant molecules are sorbed to particles in the soil matrix. The coefficient of retardation (R) was estimated by the method described in Section 4.5.4.

The distribution coefficient (K_D) was estimated to be 0.39 L/kg by Equation 10. The fraction organic carbon (f_{OC}) was measured to be 2.1 ± 0.5%. To be conservative, a minimum value of 1% was used in the calculation. The proportionality constant (K_{OC}) used in the calculation of the retardation coefficient was 39 L/kg.

The bulk density of aquifer silty sand was calculated to be 2.10 kg/L by Equation 11 based on the moisture content of the soil (19%), the specific gravity (2.65), and the void ratio (0.50).

The coefficient of retardation was estimated to be 3.5 by Equation 9. A summary of the values used for this calculation are shown below:

K_{OC} (L/kg)	f_{OC} (unitless)	K_d (L/kg)	ρ_b (kg/L)	n (unitless)	R (unitless)
39	0.01	0.546	2.10	0.33	3.5

This coefficient can be used to calculate the velocity of the contaminant plume by Equation 12. By applying the estimate of R = 3.5, the expected range of contaminant migration velocities can be calculated as:

	Retarded Contaminant Velocity (m/yr.)
Maximum	16
Minimum	0.01
Expected	0.11

5.6 Chemical Analysis

Measurement of the soil and groundwater chemistry allows delineation of the contaminant source area and the dissolved plume. It also provides geochemical evidence of the TEAPs responsible for hydrocarbon degradation. Field measurement of the following groundwater parameters was made by probes in a flow-through cell: DO, redox, electrical conductivity, pH, and temperature. Samples for laboratory analysis were taken after these parameters stabilized during well purging. With the exception of methane analysis carried out at the University of Alberta, all laboratory chemical analyses were carried out by ETL, Edmonton utilizing the standing offer agreement with 4 Wing Cold Lake.

5.6.1 Field Groundwater Chemistry

Table 11 contains a summary of parameters measured with probes in a flow-through cell prior to groundwater sampling. Measurements can be compared to groundwater data from six selected shallow monitoring wells in central and northern Alberta summarized in Appendix C.

Measured values of pH ranged from 6.7 to 7.9 indicating that conditions are neutral and therefore are optimal for microbial growth. These values fall within the range of typical shallow groundwater in central and northern Alberta.

Electrical conductivity measurements averaged approximately 1100μS/cm with anomalous low readings of approximately 600μS/cm at 167-3 and MW-14A and a peak reading of 2690μS/cm at CF-5. The anomalous values suggest that the groundwater in these wells may have come from a different source than the rest of the groundwater analyzed at the site. These readings appear to be at the high end of the typical range of conductivity values in shallow wells in the region.

Redox potentials were measured to evaluate redox conditions in contaminated aquifers. Redox potentials ranged from -75mV up to -35mV revealing slightly reducing conditions in the subsurface environment. The measurements appear typical of shallow groundwater in the region.

Groundwater temperatures monitored in the flow-through cell did not provide adequate accuracy because the water was warmed during sampling. A more precise measurement of the groundwater temperatures was conducted in October 1998 by lowering a temperature transducer directly into selected monitoring wells. Average measured groundwater temperatures at the site were 8.5°C with a maximum of 9.8°C and a minimum of 7.2°C. These values average approximately 2.5°C warmer than shallow groundwater measured at other wells in central and northern Alberta (Appendix C).

Dissolved oxygen levels will be discussed in the context of TEAs in section 5.6.3. Results indicate that the DO levels lie within the typical range for a contaminated site.

5.6.2 Contaminant Assessment Results

The contaminants of concern analyzed in soil and groundwater for this study were BTEX. These compounds are the most soluble of all fuel constituents (Table 3) and are known to have both chronic and acute health effects in humans and aquatic organisms (ASTM, 1995). In addition, laboratory analysis included volatile (C5 - C10) and extractable (C11 - C30) hydrocarbons.

Analysis were performed on 21 groundwater samples and 9 soil samples. The chemical analysis results for the soil and groundwater from the June, August, and October sampling periods are contained in Table 12. Figures 45 and 46 show the spatial distribution of BTEX concentrations measured in soil and in groundwater samples. The dissolved contamination appears to be associated with sandy lenses or layers within the clay till. These layers are likely hydraulically linked to two separate sources of hydrocarbon contamination: backfill sand from around the former storage tanks (possibly intercepted in MW-97-6) and contaminated silty sand and clay fill in the area of the former pump islands.

5.6.2.1 Soil Vapour Contamination

Soil vapour results are included in the drill logs for each auger hole (Appendix A). For all test holes, LEL levels were measured as non-detectable in the till below 4 metres depth. Peak levels of 30% were measured in AH-12 at 1.6 and 2.8m depth and in MW-14A at 3.9m depth. CO_2 levels reached 2000ppm (by volume) at 3.3m in AH-15, 1300ppm at 3m in AH-11, and 3200ppm at 3.2m in AH-12 compared to background readings in uncontaminated soil of 600-700ppm (AH-10A at 1.9m and AH-13 at 2.7m). These results correlate well with BTEX concentrations measured at similar depths in the soil and groundwater and provide supporting evidence that hydrocarbon contamination is limited to the upper 4m of the stratigraphy.

5.6.2.2 Soil Contamination

The reported detection limits for each of the BTEX compounds in soil were 0.01 ug/g [ppm] (or 10μg/kg [ppb]). CCME recommended soil quality criteria for Commercial/Industrial land

use with respect to BTEX compounds in soil are 5, 0.8, 20, and 17 ug/g (ppm), respectively. For Residential/Parkland land use, the values are 0.5, 0.8, 1.2, and 1 ug/g (ppm), respectively (CCME, 1997).

Detectable levels of BTEX were measured between 2.0-4.0m depth in auger holes AH-12, AH-14, and AH-23. At AH-12, a sample at 3.0m depth contained 54, 380, 71, and 420 ug/g [ppm] BTEX respectively, but at 4.9m depth the concentration had declined to 0.02, 0.11, <0.01, and 0.22 ug/g BTEX. This contamination resided at the base of fill material that was located near the former pump islands. In AH-14 the peak concentration was measured at 3.9m, with levels of BTEX measured at 5.1, 77, 24, and 150 ug/g respectively. Soil from AH-23 was sampled with a solid stem auger rather than the split spoon used for the other samples. This increased the degree of disturbance to the soil, which may have permitted some of the BTEX to volatilize. A sample at 2.0m depth contained <0.01, <0.01, 0.10, and 1.7 ug/g BTEX, respectively.

Soil sampled from AH-10 (upgradient, to the south), AH-11 and AH-15 (to the east of the source), and from AH-13 (to the west of the source) did not contain detectable BTEX concentrations.

TEH and TVH levels were measured in 3 samples: AH-11 at 4.0m, AH-14 at 3.1m, and AH-15 at 2.4m. The sample from AH-11, which did not exhibit a hydrocarbon odour, contained 22 and <0.5 ug/g [ppm] TEH/TVH, respectively. Samples from AH-14 and from AH-15 both exhibited moderate to strong hydrocarbon odour and contained 35/210 ug/g and 14/<0.5 ug/g TEH/TVH, respectively.

5.6.2.3 Groundwater Contamination

The detection limits for BTEX in water are approximately 10 times less than those in soil, at 0.001 mg/L [ppm] (or 1µg/L [ppb]). CCME interim quality criteria for drinking water (Canadian Council of Resource and Environment Ministers (CCME), 1995) for the BTEX compounds are 5, <24, <2.4, and <300 µg/L (ppb), respectively. For freshwater aquatic life the values are 300, 300, 700, and undefined µg/L (ppb), respectively. There are no values listed for livestock watering or irrigation for these compounds. These values are not well suited for remediation criteria for this

commercial site, as the groundwater is not used for any of the stated applications. However, they do provide an indication of the magnitude of possible acceptable concentrations for the compounds.

Dissolved phase BTEX was measured at peak values in monitoring well 97-6 at 17000, 26000, 2600, and 21000 ug/L [ppb], respectively. These values are approximately one half of the maximum equilibrium dissolved BTEX concentration that can be expected for water in contact with gasoline (Wiedemeier et al., 1995). The borehole logs indicate that this well intercepted a 1.5m thick sand layer at 2.5m depth (AGRA Earth & Environmental, 1997). Previous work (Geo-Physi-Con Ltd., 1991; Environment Canada - Federal Programs Division, 1995) has indicated that the original underground petroleum fuel tank was at this approximate location, suggesting the sand may be the remains of backfill surrounding the original tank (Figures 36, 38, 39). A contaminated gravelly sand layer was detected approximately eight metres to the northeast in MW-14A and AH-14 that may represent a discontinuous sand seam at a depth of approximately 3.8-4.2m which connects with the backfill. Groundwater analyzed in MW-14A contained 5400, 280, 37, and 120 ug/L of BTEX, respectively.

Groundwater tested in monitoring wells F(167-1B), G(167-1A), 97-3, and bailed from AH-12 also contained significant levels of BTEX contamination. The BTEX measured in 97-3 and AH-12 may be associated with hydrocarbons spilled near the pump islands and the BTEX measured in wells F and G may be due to contaminant migration within the buried utilities. BTEX were not detected in monitoring wells CF-5 (TH205), 9109-9(TH-206), H, and 97-2.

Duplicate analyses were carried out on groundwater sampled in June from 97-3 as a check on laboratory quality assurance, and the results showed good agreement (6530 ppb and 6190 ppb total BTEX). The well was resampled again in August, and although BTEX levels were about half that indicated in June (3068 total BTEX), the ratio of concentrations between the BTEX constituents was similar. Rinsate blanks and duplicates were also analyzed at the FFTA site and during a concurrent investigation at the former base landfill (Biggar and Mullick, 1999). These results also validate the sampling technique and the laboratory analysis.

Some of the monitoring wells sampled were screened over intervals up to 5.0m in length (incl. 97-6, 97-3), which could dilute BTEX concentrations with uncontaminated groundwater from a different elevation. Groundwater below 6.0m depth was not investigated. All wells with detectable BTEX contamination were within an area approximately 40m x 40m (Figure 46).

5.6.3 Electron Acceptor Analysis

To determine if microbial degradation of the contaminants is ongoing in the groundwater, analysis of the depletion of TEAs was performed. The TEAs analyzed in this study were dissolved oxygen (DO), sulfate (SO_4^{2-}), and nitrate (NO_3^-), which is first reduced to nitrite (NO_2^-) and finally to nitrogen gas (N_2). In addition the by-products of microbial degradation of organic compounds were analyzed in this investigation, and include iron (II) (Fe^{2+}), sulfide (S^{2-}), and methane.

Figure 47 summarizes selected geochemical data from the site in a traverse parallel to the direction of groundwater flow. Levels of DO were depleted from 3-4mg/L background levels to <1mg/L in the source area. The concentration gradually increases downgradient proportionally to the decreasing contaminant levels. Nitrate and nitrite concentrations were not detected at any of the wells tested in this study. Iron reduction was evidenced by levels of dissolved iron at a maximum (26.5mg/L) within the source area and at non-detectable levels downgradient. Unfortunately, the background Fe^{2+} sample could not be analyzed, but the presence of 3.5mg/L DO suggests that conditions were not favourable for the reduced form of iron to be present. Sulfate concentrations decreased from a background level of 14.8mg/L to 9.7mg/L through the source area. Surprisingly, sulfate levels jump to 150mg/L farther downgradient. This high level was also measured in MW-CF-5 (200mg/L) and indicates that a source of sulfate is present downgradient of the contaminant source area. Sulfide levels were non-detectable outside the plume and reached a maximum of 0.02mg/L within the source area (not plotted on Figure 47 due to scale). Dissolved methane gas was not detected outside the plume area and concentrations reached a maximum of 1.6mg/L immediately downstream of the source area. This indicates methanogenic activity is likely occurring within the plume.

5.6.4 Contaminant Mass Balance through Stoichiometry

An estimate of the contribution of each redox process to the total contaminant mass biodegraded can be achieved by applying the stoichiometry of the chemical reactions describing the oxidation of BTEX (Equations 1-5, Section 2.1). Based on these relationships, the mass ratio of TEA required to oxidize an equivalent amount of BTEX can be calculated. Metabolic by-product concentrations (Fe^{2+}, CH_4) can be correlated to the mass of BTEX degraded in the same fashion. A summary of the mass ratios for TEAs or metabolic by-products to total BTEX degraded is included as Table 13 (the ratio is averaged for each BTEX constituent). By assuming that the change in each electron acceptor/metabolic by-product concentration across the contaminated site is due solely to the biodegradation of BTEX, the relative contribution of each redox process can be assessed. The results of this analysis are summarized in Table 13 and indicate that anaerobic processes are the most significant. As discussed in Section 4.6.4, methanogens only degrade the by-products of other degradation reactions and therefore the amount of BTEX degraded by this stoichiometric relationship (Equation 5) should not be considered a separate mechanism that uniquely contributes to the total amount of BTEX degraded. The amount of BTEX degraded by this stoichiometric relationship most likely represents the total capacity for both aerobic and anaerobic BTEX degradation at the site. If it is assumed that the total BTEX biodegradation capacity can be calculated based on the concentration of dissolved methane alone, then the ability to degrade approximately 2.1mg/L BTEX per litre groundwater exists at the site. If it is assumed that aerobic respiration, iron (III) reduction, and sulfate reduction can be added together to account for a combined BTEX degradation capacity, then the geochemical data suggest that the site has the ability to degrade approximately 3.4mg/L BTEX per litre groundwater by these TEAP. The total calculated BTEX biodegradation capacity of approximately 3mg/L is less than the measured maximum BTEX concentration (64.6mg/L), suggesting that the biodegradation capacity at the site is not adequate.

5.7 Microbial Analysis

Another line of evidence for intrinsic bioremediation is provided by an investigation of the *in situ* microbial community. A laboratory test was performed to enumerate microbes from a soil sample at the site by classifying them into broad categories based on the method they use to obtain their energy for metabolism. Direct measurement of microbial activity by a laboratory microcosm experiment was also performed to analyze the rate and extent of microbial activity under different environmental conditions.

Samples of the silty clay soil were taken for microbial analysis from at or below the water table at 4 locations:

- upgradient: AH-10 at 3.0m depth;
- within the contaminated zone: AH-14 at 3.9m depth;
- within the contaminated zone (rate study sample): AH-23 at 2.0m depth;
- downgradient: AH-11 at 4.0m depth.

5.7.1 Microbial Enumeration

Enumeration of microbes permits an analysis of the population of microbes present in the soil at the site. This information provided evidence of the dominant TEAPs and confirmed the presence of microorganisms capable of degrading hydrocarbons.

The most probable number (MPN) technique was employed for soil microbe enumeration. This approach is widely used in microbiology and provided a straightforward and simple means of making an order of magnitude scale estimate of the quantity and type of microorganisms present at the site.

5.7.1.1 Enumeration Methodology

This method utilizes statistical analysis of bacterial growth counts in replicate test tubes containing a serially diluted sample. Soil samples were gathered in the same manner as for chemical analysis at locations upgradient (AH-10), within (AH-14), and downgradient (AH-11) of the contaminant source area. Serial dilutions up to 10^{-7} were prepared in the same manner and

with the same liquid media as used at the FFTA site, which is described in Section 4.7.1.1. Appendix G contains details of the MPN calculations and the liquid media recipes. The test tubes were incubated at 6°C for 4 weeks and then 2 weeks at 22°C, and were scored weekly for positive results.

5.7.1.2 Enumeration Results

As indicated in Figure 48, significant populations of microorganisms were detected at the site in the order of 10^5 to 10^7 total heterotrophs/gram dry soil. Hydrocarbon degraders were also detected at significant population levels varying from 10^4/g background and downstream down to 10^2/g within the plume. The MPN test for hydrocarbon degraders was conducted under aerobic conditions; it is therefore likely that the low number of aerobic organisms detected near the source area is an indication that the dominant biodegradation process there is anaerobic. The dominant family of microorganisms enumerated were the nitrate and nitrite reducers, which were measured at 10^5 to 10^7/g. The lack of dissolved nitrate and nitrite detected in the groundwater suggests that the site may be nitrate limited. Many denitrifying bacteria are facultative (able to survive in both an aerobic and an anoxic environment) and may be surviving through utilization of an alternate TEA.

Microorganisms capable of iron reduction were detected at measurable levels at all microbial sampling locations. Sulfate reducers (SRB) were not detected despite geochemical evidence suggesting that sulfate reduction is occurring. A similar phenomenon occurred nearby during a study at the main fuel storage compound in 1997. It is possible that sulfate is being reduced in the groundwater by another process or that the SRB were not successfully cultured, as they are very sensitive to their anoxic environment.

5.7.2 Microbial Activity

A radiorespirometric laboratory investigation was carried out on soil sampled within the hydrocarbon plume in order to study the rate and extent of toluene mineralization. The purpose of the investigation was to confirm the potential and assess rates for biodegradation under the cold temperature conditions at the site. A known amount of radiolabelled toluene was added to

serum vials containing a slurry of soil and groundwater from the contaminated zone. The appearance of radiolabelled carbon as carbon dioxide ($^{14}CO_2$) in the vials provides direct evidence for the microbial biodegradation of the radiolabelled toluene. Measuring the $^{14}CO_2$ concentration increase with time indicated the rate of biodegradation and rate constants were then calculated.

5.7.2.1 Methodology for Microbial Activity Experiment

The soil from AH-23 was mixed at a ratio of 1kg soil to 1L groundwater obtained from monitoring well 97-6 (adjacent to the sample site) prior to addition to the serum vials. Only one environmental condition was tested for this sample, which was in an aerobic headspace incubated at 8°C. All other aspects of the preparation and measurement of the batch study vials were identical to those described for the FFTA samples in Section 4.7.2.1.

5.7.2.2 Trends in Biodegradation Rate Study Data

The same trends that were noted in the FFTA samples are apparent in the soil sampled from this site (Figure 49). The samples exhibited a brief lag period of limited $^{14}CO_2$ production, followed by a period of rapid $^{14}CO_2$ evolution. Following the rapid mineralization stage, $^{14}CO_2$ production slowed dramatically as conditions likely became limited by the availability of substrate, nutrients, or TEAs. This sample exhibited a moderately fast mineralization rate and conversion to $^{14}CO_2$ reached approximately 50% at the maximum extent. The rest of the ^{14}C toluene may have been converted to microbial biomass with smaller amounts persisting as intermediate degradation products and unconverted toluene. The nutrient-amended controls did not exhibit $^{14}CO_2$ concentrations significantly different than the non-amended samples (Figure 12). This suggests that the microbial degradation of contaminants at the site is not likely nutrient limited.

Since these trials were carried out under conditions similar to those existing in the field, the results provide strong evidence for biodegradation of BTEX at the site under *in situ* temperatures.

5.7.2.3 Simple First Order Rate Interpretation

The biodegradation process was modeled by first order kinetics, as described in Section 4.7.2.4. A plot of Ln (C_t) versus time yielded a line whose steepest slope can be interpreted as the maximum rate constant, k. By assuming that 50% of the ^{14}C radiolabelled toluene remained unconverted (the greatest recovery as $^{14}CO_2$ was 47%), the amount of toluene remaining at any time may be calculated as [100% - (2 x $^{14}CO_{2\ measured}$%)] (Figure 50). In order to compare the rate constant with those calculated for the FFTA samples, it is necessary to assume that 68% of the sample was recovered and calculate the amount of toluene remaining as [100% - (100/68 x $^{14}CO_{2\ measured}$ %)] (Figure 51).

By assuming that 50% of the toluene added to each vial remains unconverted, the half-life calculated for toluene under aerobic conditions at 8°C is approximately 0.03 years. By assuming that only 32% of the toluene remained unconverted, the half-life is calculated to be 0.04 years. The small difference between the half-lives illustrates that this assumption does not significantly affect the interpreted biodegradation rate. These values are both at the lower end of the reported range for toluene (ASTM, 1995) suggesting that these microbes are well acclimated to their environment. The results are summarized in the table below.

First Order Biodegradation Rate Estimate

Sample	Rate Constant, maximum k (day^{-1})	Rate Constant, maximum k (yr^{-1})	Half Life, $T_{1/2}$ (yr)
Aerobic, 8°C (Assume 50% Recovered)	0.075	27	0.03
Aerobic, 8°C (Assume 68% Recovered)	0.044	16	0.04
Reported Range (ASTM, 1995)	-	4.0-35	0.02-0.17

5.7.2.4 Alternative Models for Activity: The Declining Growth Model

As discussed in Section 4.7.2.5, the application of more complex models to experimental data can permit a more rigorous comparison of the data pattern. The Declining Growth model was applied to the data set to quantitatively compare the reaction rate, the lag time, and the extent of mineralization for the contaminated soils incubated at different temperatures.

This model is particularly useful as it takes into account the decreasing rate of growth with time that is evident in the experimental data (Figure 52). To account for substrate taken up by the microbes, it was assumed that the amount of ^{14}C-toluene that was actually degraded was twice the amount detected as $^{14}CO_2$. Therefore, the model was fit to $2x^{14}CO_2$ (detected) and the model parameters C_{max} and k were determined for the transformed dataset by the method of least squares. The lag period was accounted for by forcing the start of the model curve through time = 7 days. This value was determined with a trial and error approach by minimizing the sum of the squared residuals. The model provided a good fit to the data (R^2 = 0.99) and the random scatter of residuals over a small range confirmed its validity (Appendix I). The parameter C_{max} defines the extent of mineralization for the sample to be approximately 41%, which is nearly identical to the FFTA aerobic sample incubated at 8°C (42%). The predicted biodegradation half-life was 0.024, which is also nearly identical to the FFTA aerobic 8°C sample (0.023). Further discussion of the microcosm experimental results is included as Section 6. The Declining Growth model parameters are summarized below:

Declining Growth Rate Model Parameters

Sample	Lag Period (days)	C_{max} (% $^{14}CO_2/^{14}C_T$)	k (yr^{-1})	$t_{1/2}$ (yr.)	R^2
OIS Aerobic 8°C	7	40.7	29.4	0.024	0.99

5.8 Groundwater Modeling

An analytical computer model was used to estimate the extent of contaminant migration at the site if no engineered remediation technique was applied (e.g. no source removal). BIOSCREEN is computer software that was designed to evaluate the potential for intrinsic bioremediation and is distributed free of charge via the US EPA web site (USEPA, 1999). The program works within a spreadsheet program and calculates plume centreline concentrations as output.

The modeling problem was approached by first calibrating the prediction of current contaminant concentration against field data by adjusting the apparent first order biodegradation

constants. A range of values for hydraulic conductivity, retardation, and dispersivity were used in the model that accounted for the variability in field measurements and heterogeneity at the site. The calibrated model was then used to predict the future plume centreline concentrations.

The modeling results should be recognized as only a general approximation of site conditions, and are limited in applicability by the heterogeneity of the subsurface at the site. The predicted contaminant migration rate may be considered secondary to the risk associated with the plume intercepting the drinking water supply lines at the site (discussed later).

5.8.1 Site Conceptual Model

The site conceptual model has not yet been resolved because, despite being a rather small site, the local conditions are highly heterogeneous. In a number of boreholes, a relatively thin gravelly/sandy layer (approximately 0.3m or less) was encountered at a depth between 2.0 to 4.0m. The presence of hydrocarbon contamination at the site appears to be confined to this sandy layer near the former petroleum storage tanks and also to silty clay and sand fill in the area of the former pump islands (as discussed in Section 5.6.2). The sandy layer is not, however, continuous across the site, as it was not encountered in some of the boreholes drilled during this investigation (AH-11, AH-13, and AH-22). Upgradient from this site at the main Petroleum, Oil and Lubricant (POL) compound there is a sand layer, approximately 4m thick, beneath approximately 2m of clay. It is speculated that the sand layer at the POL compound tapers out as the ground surface slopes down to the Old Imperial site. The thin discontinuous sand at the Old Imperial site may be hydraulically connected to the upper sand layer at the POL compound. This is somewhat supported by the fact that the thin sandy layer resides a few metres below the water table at the Old Imperial site.

Because the thickness and lateral extent of the sandy layer in the vicinity of the old storage tanks is not yet resolved (further delineation is recommended as outlined in Section 5.9.1), the assumed geologic stratigraphy can lead to two quite different site models. If it is presumed that the sandy layer at approximately 3.5m depth is laterally extensive, then a high rate of biodegradation must be assumed in order to account for the limited migration of dissolved contaminants (Scenario A). If it assumed that the layer is not laterally extensive however, and

that transport of contamination is dominated by migration in unconnected lenses of sandy material and weak connections to underground utilities backfill, then a much lower rate of biodegradation must be assumed (Scenario B).

Supporting evidence for Scenario B comes from a variety of sources. The thin sandy layer intercepted in MW-14, while certainly contaminated, was not hydraulically well connected to the rest of the aquifer. This is evidenced by the extremely slow response of the water level in the well during slug testing and also by the low recharge observed during development of the well. Great care was taken during the hollow stem drilling investigation to seek out conductive layers within the till, but only limited amounts of coarse grained material were intercepted. The analysis of TEAPs indicated that anaerobic processes dominate biodegradation at the site, which are orders of magnitude slower than the aerobic biodegradation of hydrocarbons (Wiedemeier et al., 1995).

Given the uncertainty, both scenarios for site conditions were modeled. For Scenario A, the estimate for seepage velocity reflects the higher conductivity in silty sand and consequently large biodegradation component required to calibrate the model to field measurements of contamination. The estimate of seepage velocity for the second conceptual model (Scenario B) is representative of fractured, weathered clay till as estimated in Section 5.5.2.

5.8.2 BIOSCREEN Code Overview

BIOSCREEN calculates the two dimensional transport of a solute in groundwater by considering advection, dispersion, retardation, and biodegradation. Vertical migration can be considered by inclusion of a vertical dispersivity constant. Advection, dispersion, and retardation are uniformly applied as constant across the aquifer. Biodegradation is calculated by two methods in BIOSCREEN; either by the inclusion of a first order degradation rate constant, or by accounting for the change in electron acceptor concentration across the site and assuming an instantaneous reaction between TEA and BTEX. Both approaches were used in this modeling exercise. A detailed explanation of the equations used can be found in the BIOSCREEN manual (Newell et al., 1997). Because it accounts for the change in electron acceptors/by-products at the site, the instantaneous reaction model is considered to provide a more accurate prediction of

biodegradation than the first order degradation model (Connor et al., 1994). For this reason, while both approaches were used, the predictions of the instantaneous reaction model were considered the more representative results.

5.8.3 Model Assumptions

A number of assumptions are required in order to apply this model. The following assumptions should be considered when interpreting the model predictions:

1. Darcy's Law is valid and hydraulic head gradients are the only significant driving mechanism for fluid flow.
2. The porosity, hydraulic gradient, and hydraulic conductivity of the aquifer are constant with time and space.
3. Gradients of fluid density, viscosity, and temperature do not affect the velocity distribution.
4. Ionic and molecular diffusion are negligible contributors to the total dispersive flux.
5. Vertical variations in head and concentration are negligible.
6. The aquifer is homogeneous and isotropic with respect to longitudinal and transverse dispersivity.
7. Biodegradation can be approximated as either an instantaneous reaction or with a first order degradation rate.

For the purposes of this preliminary modeling exercise, these assumptions are deemed reasonable. It should be noted however, that the complicated subsurface stratigraphy due in part to the utilities that cross the site might significantly affect the contamination migration pathway. These influences are difficult to model, and the results of this exercise should be considered only as a rough approximation to evaluate the actual site conditions.

5.8.4 Model Input

In BIOSCREEN, the distribution of contaminant source concentration is applied over a fixed length and depth, which is infinitely thin in a plane perpendicular to groundwater flow. The vertical plane can be broken into a maximum of five zones, allowing three different symmetrical source concentrations to be entered (see Figure 53). Estimation of the concentration and width

of each zone was made based on the BTEX contaminant contour plot (Figures 45-46). For this exercise, three zones were assigned to define an infinite hydrocarbon source. The peak concentration (zone 2) was assigned a value of 63 mg/L over 4.9m (16 feet) width, while the outer zones (1 and 3) were each approximated at 15 mg/L over 9.4m (31 feet) width. For the model scenario based on the laterally extensive sand layer (Scenario A), the contaminant source thickness was set to 0.3m (1ft). For Scenario B, the thickness of the contaminant source was estimated to be more diffuse, at 1.5m (5 feet). This prediction is based on the approximate thickness of contamination intercepted in boreholes at the site.

The gradient and porosity estimated for both sites was 0.035m/m and 0.25 as discussed in Section 5.5. The hydraulic conductivity estimated for Scenario A was $1x10^{-3}$cm/s (Freeze and Cherry, 1979), which resulted in a seepage velocity calculated to be 44m/yr (145 ft/yr). For Scenario B, the hydraulic conductivity was initially estimated at $1x10^{-5}$, as discussed in Section 5.5.2, which results in a seepage velocity of 0.4m/yr (1.4 ft/yr).

The coefficient of retardation was conservatively estimated to be 1.0 for Scenario A and 1.5 for Scenario B. The lower estimate for Scenario B reflects that the contaminant migration is expected to be in a silty sand material, which typically contains a lower organic content and a lower coefficient of retardation.

For both scenarios, the dispersivity was set to 2.1m (7.1 feet, longitudinal), 0.2m (0.7 feet, transverse), and 0.03m (0.1 feet, vertical). These values were estimated based on the size of the plume (Newell et al., 1997). BIOSCREEN predictions are highly sensitive to dispersivity estimates (Thielmann, 1997), particularly the vertical dispersivity constant.

The change in electron acceptors entered to account for the instantaneous biodegradation reaction model were as follows: 3.5 mg/L DO, 0 mg/L NO_3, 26.5 mg/L Fe^{2+}, 5 mg/L SO_4, and 1.6 mg/L CH_4. These values were selected based on the peak change in concentration between groundwater sampled upgradient and within the source area. These values accounted for an instantaneous biodegradation capacity of 5.45 mg/L BTEX, as discussed in Section 5.6.4.

5.8.5 Model Calibration

In order to calibrate the model, the simulation time was set to 40 years, which is the approximate time period between the introduction of the source and the current conditions. The parameters which were adjusted to fit the field data were the first order biodegradation constants for both scenarios and the hydraulic conductivity estimate for Scenario B.

The first order biodegradation constants measured in the laboratory experiment (Section 5.7.2.3) were not applied due to the difference often noted between the field and laboratory measured rates, as discussed previously. The values for the first order constant were adjusted, in a trial and error fashion, until the predicted contaminant concentration curve resembled the field data. Particular attention was paid to the downgradient limit of the plume during calibration.

The estimate for hydraulic conductivity was only accurate over an order of magnitude. In order that the concentration curve for Scenario B more closely fit the field data, the hydraulic conductivity estimate was increased to $2x10^{-5}$ cm/s. This increased the estimate of v_s slightly to 0.9m/yr(2.9 ft/yr), which increased the concentration predictions above the field data estimates and permitted a minimal component of biodegradation to be assigned. While it was possible to slightly increase the estimate of v_s even further and assign a larger component of biodegradation, this was not carried out because it is considered by Scenario B. The input data and predicted plume centreline concentrations for Scenario A and B is shown in Figures 54A/B and 55A/B, respectively.

For Scenario A, the first order biodegradation constant that caused the predicted curve to closely resemble the field data was $3.5yr^{-1}$. Wiedemeier, *et al.*, (1995) have published first order biodegradation constants that were determined based on calibrated field data. They range from 0.073-15 yr^{-1}, which indicates that the constant predicted for this scenario falls at the high end of the scale. For Scenario B, the biodegradation constant that best calibrates the prediction to field data is 0.069 yr^{-1}, which is below the low end of the expected range of values.

5.8.6 Model Predictions

Model predictions for Scenarios A and B were generated by adjusting the model time interval in a trial and error fashion to assess the maximum extent of the plume estimated by the instantaneous reaction model. The Scenario A predicted concentration of BTEX along the plume centreline in 100 years is shown as Figure 56. The model predicts that the plume has already reached a steady state condition (the maximum extent of the plume has been reached). It can be seen that concentrations have not been significantly reduced and the plume will likely persist for many more decades. The predicted plume centreline concentrations for Scenario B in 100 years are shown as Figure 57. The model predicts that the plume will continue to gradually expand for hundreds of years. At that time, the plume has expanded from 30m (90 feet) to over 80m (270 feet).

An important assumption that was made in this modeling exercise was that the mass of hydrocarbon source did not decay with time. This is a very conservative assumption and can have a dramatic influence on the predicted extent of the plume. It can also be assumed that there is a finite mass of organics in the source zone present as free phase or residual NAPL which dissolves slowly according to a first order process as fresh groundwater is passed through. BIOSCREEN is able to calculate predicted plume concentrations by accounting for a first order decay of the source (Newell et al., 1997). For a source half-life estimated at 100 years (source zone concentration decreased by half every 100 years), the model predictions were recalculated and are shown as Figures 58 and 59. It can be seen that the predicted concentrations in the plume have dramatically decreased from that without source decay (Figures 56 and 57). The selection of a 100 year half-life for the decay of source concentration is purely hypothetical and it has been suggested that modeling of source decay as a first order process may only be valid for low levels of contamination (Connor et al., 1994). Despite this, the exercise demonstrates the importance of source concentration on the extent and size of the dissolved plume.

5.8.7 Summary of Model Results

These model predictions are based on general approximations of site conditions and given the heterogeneous nature of the site, should not be considered highly accurate. Modeling results suggest that the contaminant plume will likely persist for many years, regardless of whether or not it has reached a steady-state condition. The persistence, extent, and level of contamination will likely be dramatically lowered if the source concentration is reduced.

5.9 Closure

Although the lateral extent of the contamination appears to be small, the presence of buried utilities complicates a thorough site characterization. Further, there has been evidence that free phase hydrocarbon contamination may be in contact with the buried water line at the perimeter of the site. The water line is likely made of polymers (HDPE or PVC, likely PVC) and there is a growing body of evidence to show that BTEX can diffuse through polymer membranes at relatively rapid rates (Boratynec and Biggar, 1998). For HDPE pipe, mass flux rates of BTEX through the pipe wall have been calculated to be approximately 36 $mg/m^2/hr$ (Park and Nibras, 1993). Given that the water is moving through the pipe, the concentration in the water will likely be nondetectable at these flux rates. If the water becomes stagnant, however, the build-up of BTEX is possible.

Samples of water were taken from the nearby fire hydrant during this investigation. The hydrant is on a small branch line that contains stagnant water. The water had considerable suspended sediment (likely rust) and had a barely measurable level of BTEX (~2μg/L). The Environmental Technician at 4 Wing subsequently took water samples from taps at residences and found no detectable BTEX. Hence, there does not appear to be BTEX above drinking water standards in the water supply due to contamination at the Old Imperial site, but there exists the potential for small amounts to enter the supply. Given the above, source removal should be considered as detailed in the following sections.

The capacity for natural attenuation of BTEX at the site appears to be inadequate to serve as the only contaminant remediation approach. The removal of the high concentration of

BTEX in the source area should be considered, with natural attenuation used as a polishing step to remove dissolved contamination remaining at the site. Based on a survey of available technologies, there are two approaches that would likely achieve the required contaminant removal: excavation and landfarm treatment of soil in the source area, or vacuum-enhanced contaminant recovery via a dual phase pumping system.

5.9.1 Cone Penetrometer Testing (CPT)

Regardless of the method chosen to treat the contaminated source area, a survey of the subsurface via cone penetration tests could provide many benefits. Cone testing provides a quick and relatively inexpensive method of delineating subsurface geological trends. A CPT investigation would improve delineation of the gravelly-sand layer that is believed to contain the bulk of the hydrocarbon contamination. The layer is too thin and/or stony in some areas to be accurately delineated with either hollow stem or solid stem auger test holes and is discontinuous. Testing on a 10m grid spacing over an approximately 40 x 40m area (25 – 4.5 m deep holes) could be completed in approximately 1.5 days. This work would cost approximately $6000, which includes the cost of mobilization (Woeller, 1999).

The refined stratigraphic model would help indicate which remedial approach would likely be the most efficient and effective. If the contaminant bearing sandy layer is relatively continuous over the site, vacuum extraction may be the most effective approach. The refined conceptual stratigraphic model could then be used to optimize the vacuum extraction system (discussed below). If cone penetrometer results indicate that the contamination is in isolated sandy pockets within the till, the results could be used to optimize the excavation of the soil (i.e. reduce the volume of soil to be hauled and treated). The presence of contaminant may possibly be further delineated at the site through the use of ultra violet induced fluorescence (UVIF) technology. The UVIF Cone Penetrometer is a standard cone tool that contains an additional module, which emits ultra violet light. This light induces a fluorescence of organic contaminants contained within soil, the intensity of which can be read with a UVIF detector on the same module. The effectiveness of this specialized detector is limited to free phase hydrocarbon contamination, so will only work in certain circumstances.

5.9.2 Excavation and Landfarm Treatment

The excavation and landfarm treatment of contaminated soil is a favourable option considering base personnel have experience with this methodology and have a landfarm available on the base. Based on existing field information, up to 40x40x4m deep of soil (6400m^3) may have to be excavated to effectively remove the bulk of the residual hydrocarbons. A fraction of this amount, perhaps less than 20%, will have to be treated at a landfarm. Both the volume of soil to be excavated and the fraction considered contaminated may be revised downwards if the cone penetration investigation indicates a thinner or shallower contaminated area.

5.9.3 Vacuum-Enhanced Recovery

Another option for contaminated source material removal is vacuum-enhanced recovery via pumping wells. This approach will likely require the lowering of the water table across the site by 1.0-1.5m to permit the vacuum extraction system to remove hydrocarbon vapours from the gravelly sand layer. The system can be used to enhance the direct removal of LNAPLs and dissolved constituents in the groundwater. It is most effective, however, when used to draw down the water table and remove volatile contaminants in the vapour phase. Mass transfer and removal of gasoline constituents can be 10,000 times more efficient in the vapour phase than in the soluble water phase (Palmer, 1996). The system also provides additional oxygen to the subsurface, which can enhance *in situ* aerobic biodegradation. The low permeability of the clay till at the site will likely facilitate dewatering and the creation of a vacuum. Should this option be considered further, a pilot test should be carried out to ensure a significant capture zone can be generated by the pumping wells and that adequate contaminant mass removal can be achieved cost effectively.

Rather than installing individual wells, an option that should also be explored is a trench system. In this configuration an L-shaped trench would be excavated along the north and east sides of the site, near to the buried water lines, but closer to the source area. The trenches would go to a depth just beneath the sandy layer. A layer of crushed stone would then be placed in the trench thick enough to intercept the sand layer, and a number of wells set into the stone layer.

The trench would be backfilled with clay, and some measures taken to prevent short-circuiting of air from the surface through the clay to the well screen. The wells would then be connected to the vacuum blower. Such a system has the advantage of a large contact area, and thus more rapid and effective mass removal. It also serves as a cut-off for contaminant movement to the water line. The trench installation can confirm the stratigraphic model and is expected to compare reasonably from an expense perspective. A caution, however, is that fire fighting equipment should be readily available (perhaps on site) during the excavation given the previous trench fire.

5.9.4 Long Term Monitoring

Once the contaminant source has been removed, a long term groundwater monitoring program may be required to ensure that unacceptable levels of BTEX do not migrate off-site. Monitoring wells will have to be installed and the groundwater analyzed at prescribed intervals to ensure contaminant migration as expected. Chemical analysis of water in the drinking waterline across site is also recommended.

5.10 Conclusions for Old Imperial Site

1. Groundwater flow at the site is to the northeast, and the gradient is approximately 0.040 m/m.
2. Migration of the dissolved contaminant plume may be dominantly controlled by the preferential flow of groundwater in a thin discontinuous gravelly sand layer at approximately 3m depth and in sand around underground utilities at the site.
3. Evidence for intrinsic bioremediation of contamination includes:
    - geochemical evidence of depleted terminal electron acceptors (TEAs) and enriched products of microbial degradation in the groundwater across the site;
    - enumeration of significant populations of: total heterotrophic, nitrate/nitrite reducing, iron reducing, and JP-4 degrading microbes in soil from the contaminated area;
    - microorganisms in soil from the contaminated area exhibit the capacity to biodegrade an aromatic hydrocarbon under cold temperature conditions.

4. The capacity for intrinsic biodegradation does not appear to be adequate to serve as the only remedial solution to the site.
5. The removal of the high concentration of BTEX in the source area may allow intrinsic remediation to serve as the final polishing step for any remaining dissolved contamination at the site.

Table 10: Old Imperial Site Monitoring Well Details

Hole ID	Northing	Easting	Top of Pipe Elev.	Depth of Screened Interval (m)
CF-3 (E)	6029953.428	547712.821	538.285	?
9109-1	6029961.055	547743.204	538.085	1?-6.0
CF-2 (D)	6029974.861	547747.403	537.963	?
A	6030017.958	547785.722	535.556	?
B	6030018.999	547786.768	535.481	?
C	6030020.546	547787.979	535.363	?
97-6	6030023.956	547789.402	535.711	1.0-6.0
MW-14A	6030028.529	547795.887	535.358	3.5-4.3
97-3	6030039.487	547793.844	535.331	1.0-6.0
97-2	6030046.416	547768.412	534.932	1.0-6.0
F(167-1B)	6030044.484	547803.424	534.652	0.3-3.5
G(167-1A)	6030045.496	547803.731	534.558	1?-6.5
CF-5	6030083.441	547772.268	534.084	1.5-5.5
9109-9	6030082.048	547801.722	533.909	1?-5.0
H	6030047.841	547835.001	533.966	?
9109-5	6030036.656	547852.47	534.361	?
97-1	6030047.566	547740.775	535.354	1.0-5.8
167-3	6030015.551	547799.789	535.044	2.0-4.0

Hole ID	June 15,1998		Aug 6-12,1998		Oct 2/7,1998	
	Depth to water	Water Elev.	Depth to water	Water Elev.	Depth to water	Water Elev.
CF-3 (E)	3.119	535.166	2.624	535.661	3.545	534.74
9109-1	3.448	534.637	3.275	534.81	3.457	534.628
CF-2 (D)	3.199	534.764	2.82	535.143	3.631	534.332
A	2.017	533.539	1.795	533.761	2.359	533.197
B	2.155	533.326	1.907	533.574	2.54	532.941
C	2.047	533.316	1.8	533.563	1.433	533.93
97-6	2.387	533.324	2.149	533.562	2.56	532.798
MW-14A						
97-3	2.53	532.801	2.105	533.226		
97-2	2.107	532.825	1.807	533.125		
F(167-1B)	2.46	532.192	2.857	531.795		
G(167-1A)	2.33	532.228	1.798	532.76		
CF-5	3.18	530.904	2.642	531.442	3.381	530.703
9109-9	3.48	530.429	3.019	530.89	3.709	530.2
H	2.25	531.716	1.805	532.161	2.302	531.664
9109-5	2.66	531.701	2.176	532.185		
97-1	1.886	533.468				
167-3			1.3	533.744	1.801	533.243

Table 11: Groundwater Parameters Measured in the Field at the Old Imperial Site

Monitoring Well	Screened Interval (m)	Date (1998)	DO mg/L	Temp* °C	pH	Conductivity uS/cm	Redox Potential mV
97-2	1.0-6.0	Aug	3	8.8	7.2	900	-70
97-3	1.0-6.0	Aug	0.9	8.8	6.9	1140	-35
97-6	1.0-6.0	Aug	<0.5	8.0	6.7	1360	-44
F(167-1B)	0.3-3.5	Aug	2.0	-	6.7	1148	-47
9109-9 (TH206)	1.0?-5.0	Aug	2.5	8.6	7.9	1040	-75
H	1.0?-5.5	Aug	4.3	8.3	7.6	1310	-44
CF-5(TH 205)	1.5-5.0	Aug	1.1	8.0	7.0	2690	-44
MW-14A	3.5-4.3	Oct	1.1	7.8	7.5	602	-
167-3	2.0-4.0	Aug	<1	9.8	7.2	610	-22
D (CF-2)	1?-5.0	Oct		9.3			
9109-1	1.0?-6.0	Aug	3.5	7.2			
E (CF-3)	1?-3.5	Oct		9.3			
Average			1.8	8.5	7.2	1200	-48

* Temperature measured October 1-8, 1998

TABLE 12: Chemical Analysis of Groundwater (A,B) and Soil (C) Samples from the Old Imperial Site

12 A: Groundwater Contamination

Hole I.D. units Detection Limit	Location	Date (1998)	Sampling Method[1]	Screened interval (m)	Benzene ug/L [ppb] 0.5	Toluene ug/L [ppb] 0.5	Ethylbenzene ug/L [ppb] 0.5	Xylenes ug/L [ppb] 0.5	Total BTEX ug/L [ppb] 0.5	TEH ug/L [ppb] 50	TVH ug/L [ppb] 100
97-6	near source	June	bladder	1.0-6.0	17000	24000	1800	19000	61800		
97-6	near source	Aug	bladder	1.0-6.0	15000	26000	2600	21000	64600	3200	88000
97-3	near source	June	bladder	1.0-6.0	6000	150	<0.5	380	6530		
97-3 (dup)	near source	June	bladder	1.0-6.0	5700	110	<0.5	380	6190		
97-3	near source	Aug	bladder	1.0-6.0	2900	28	<0.5	140	3068	110	3700
F(167-1B)	near source	June	bladder	0.3-3.5	7600	3300	130	2300	13330		
F(167-1B)	near source	Aug	bladder	0.3-3.5	5100	1700	220	1300	8320		
AH-12	near source	Aug	bailer	0.0-5.5	5200	15000	1800	13000	35000	1400	49000
MW-14A	near source	Oct	bladder	3.5-4.3	5400	280	37	120	5837		
G(167-1A)	near source	June	bladder	1.0(?)-6.5	240	1.7	<0.5	14	255.7		
167-3	near source	Aug	bladder	2.0-4.0	1.2	82	0.6	9.7	93.5		
97-2	downgradient	June	bladder	1.0-6.0	0.7*	1.4*	<0.5	1.6*			
97-2	downgradient	Aug	bladder	1.0-6.0	<0.5	<0.5	<0.5	<0.5	<0.5		
H	downgradient	June	bladder	1.0(?)-5.5	20*	99*	14*	110*			
H	downgradient	Aug	bladder	1.0(?)-5.5	<0.5	<0.5	<0.5	<0.5	<0.5		
CF-5 (TH 205)	well downgradient	June	bladder	1.5-5.5	<0.5	<0.5	<0.5	<0.5	<0.5		
9109-9(TH 206)	well downgradient	June	bladder	1.0(?)-5.0	<0.5	<0.5	<0.5	<0.5	<0.5		
9109-9	well downgradient	Aug	bladder	1.0(?)-5.0	<0.5	<0.5	<0.5	<0.5	<0.5		
Rinsate Blank		June	bladder		5.6	1	0.7	0.2	7.5		
Rinsate Blank		Aug	bladder		<0.5	<0.5	<0.5	0.5	0.5		

*likely cross-contaminated

[1]Method

bladder	Positive displacement bladder pump
bailer	Disposable dedicated bailer with low-flow spout

TABLE 12: Chemical Analysis of Groundwater (A,B) and Soil (C) Samples from the Old Imperial Site

12 B: Groundwater All Other Analysis

Hole I.D. units Detection Limit	Location	Date (1998)	Sampling Method*	Screened Interval (m)	Nitrate/nitrite mg/L [ppm] 0.05	Ferrous Iron mg/L [ppm] 0.1	Sulfate mg/L [ppm] 0.5	Sulfide mg/L [ppm] 0.002	Total Alk mg/L [ppm] 5	Ph/K/TKN Nutrients mg/L [ppm] 0.02/0.1/0.2	Methane mg/L [ppm] 0.1
9109-1	upgradient	Aug	bailer	1.0(?)-6.0	<0.05	0.6	14.8	<0.002	414	0.03/3.8/0.5	0
AH-15	near source	Aug	bailer	0.0-5.3	<0.05	3.5	6.1	0.020	442		1.6
97-6	near source	June	bladder	1.0-6.0							
97-6	near source	Aug	bladder	1.0-6.0	<0.05	26.5	9.7	0.02	789	0.2/8.1/1.8	0.2
97-3	near source	June	bladder	1.0-6.0							
97-3 (dup)	near source	June	bladder	1.0-6.0							
97-3	near source	Aug	bladder	1.0-6.0	<0.05	0.5	31.6	0.008	613		0.2
F(167-1B)	near source	June	bladder	0.3-3.5							
F(167-1B)	near source	Aug	bladder	0.3-3.5	<0.05	7.5	9.8	0.004	664		
AH-12	near source	Aug	bailer	0.0-5.5	<0.05	9.4	12.6	0.007	401		
MW-14A	near source	Oct	bladder	3.5-4.3	0.13	0.1	44	<0.002	416		
G(167-1A)	near source	June	bladder	1.0(?)-6.5							
167-3	near source	Aug	bladder	2.0-4.0	<0.05	6.1	0.9	0.015	391	0.32/5.5/1.5	0.3
97-2	downgradient	June	bladder	1.0-6.0							
97-2	downgradient	Aug	bladder	1.0-6.0	<0.05	0.1	100	<0.002	459		0
H	downgradient	June	bladder	1.0(?)-5.5							
H	downgradient	Aug	bladder	1.0(?)-5.5	<0.05	8.4	5.0	<0.002	574	0.35/9.6/0.7	0.6
CF-5 (TH 205)	well downgradient	June	bladder	1.5-5.5							
CF-5 (TH 205)	well downgradient	Aug	bladder	1.5-5.5	0.67	<0.1	200	<0.002	593		0
9109-9(TH 206)	well downgradient	June	bladder	1.0(?)-5.0							
9109-9	well downgradient	Aug	bladder	1.0(?)-5.0	<0.05	<0.1	150	<0.002	827		0
Rinsate Blank		June	bladder								
Rinsate Blank		Aug	bladder		<0.05	<0.1	5	<0.002	7	0.5/0.4/-	

***Method**

bladder	Positive displacement bladder pump
bailer	Disposable dedicated bailer with low-flow spout

TABLE 12: Chemical Analysis of Groundwater (A,B) and Soil (C) Samples from the Old Imperial Site

12 C: Soil Analyses

Hole I.D. units Detection Limit	Location	Date (1998)	Sampling Method*	Depth m	Benzene ug/g (ppm) 0.01	Toluene ug/g (ppm) 0.01	Ethylbenzene ug/g (ppm) 0.01	Xylenes ug/g (ppm) 0.01	TEH ug/g (ppm) 5	TVH ug/g (ppm) 0.5	Ferric Iron ug/g (ppm) 0.5
AH-10	upgradient	Aug	Split S	3.1	<0.01	<0.01	<0.01	<0.01			695
AH-11	downgradient	Aug	Split S	4.0	<0.01	<0.01	<0.01	<0.01	22	<0.5	691
AH-12	near source	Aug	Split S	3.0	54	380	71	420			
AH-12	near source	Aug	Split S	4.9	0.02	0.11	<0.01	0.22			
AH-13	near source	Aug	Split S	2.6	<0.01	<0.01	<0.01	<0.01			508
AH-14	near source	Aug	Split S	3.1	7.3	30	5.5	30	35	210	474
AH-14	near source	Aug	Split S	3.9	5.1	77	24	150			
AH-15	near source	Aug	Split S	2.4	<0.01	<0.01	<0.01	<0.01	14	<0.5	
AH-23	near source	Oct	Solid S	2.0	<0.01	<0.01	0.10	1.7			

***Method**

Split S	Sample from 3-3/8" ID Split Spoon
Solid S	Sample from 6" Solid Stem Auger

Table 13: Mass Ratio Summary of TEA Consumed or Metabolic Byproduct Produced to Total BTEX Degraded at the Old Imperial Site

Terminal Electron Accepting Process	Mass of BTEX Degraded per unit mass of Electron Acceptor Utilized* (mg)	Mass of BTEX Degraded per unit mass of metabolic Byproduct Produced* (mg)	Measured Concentration Change at the site (mg/L)	Biodegradation Capacity (mg/L)
Aerobic Respiration	0.32		3.5	1.11
Denitrification	0.21		0	0.00
Iron III Reduction		0.05	20	1.22
Sulfate Reduction	0.21		6	1.06
Combined Capacity				3.39
Methanogenesis**		1.28	1.6	2.05

* after Wiedemeier et al, 1995

**assumed total biodegradation capacity

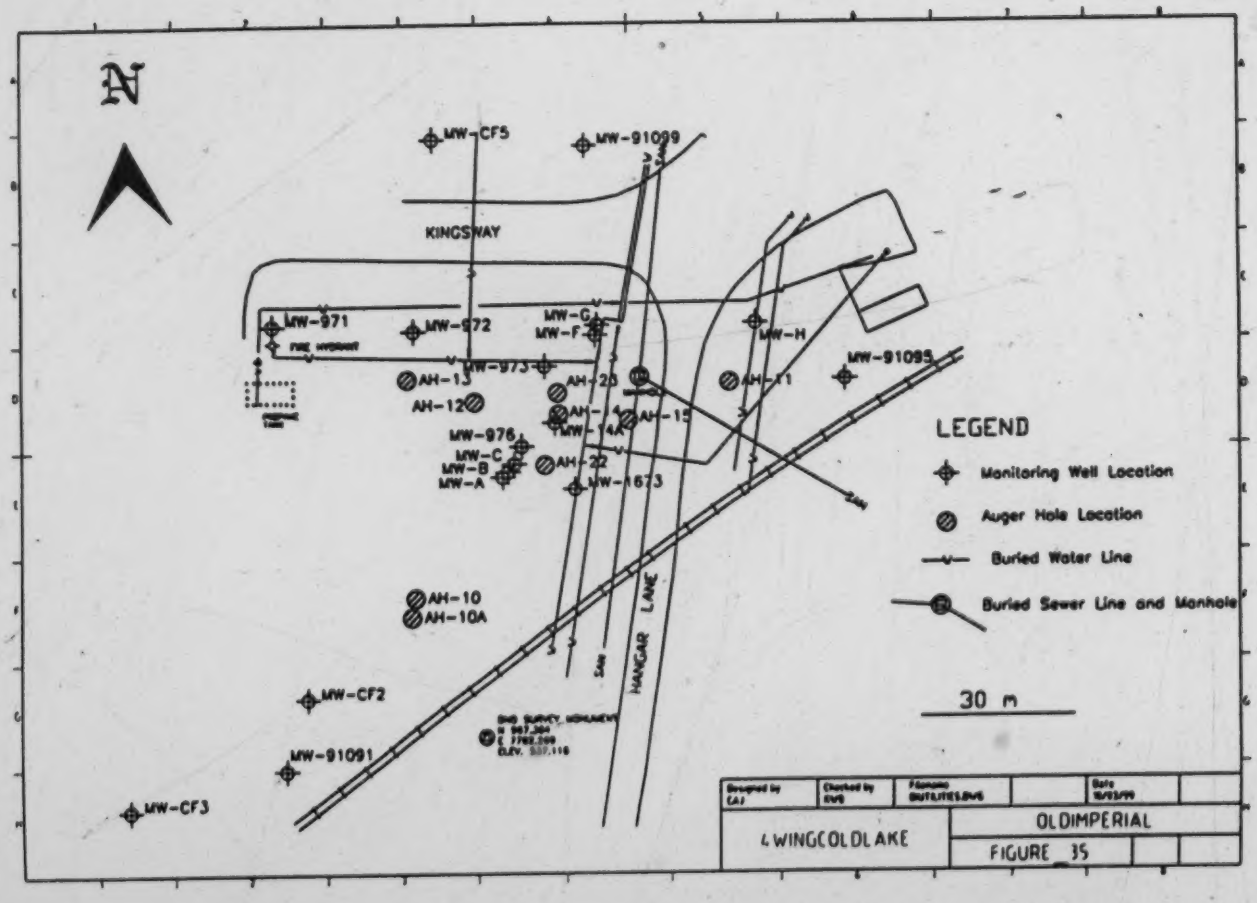
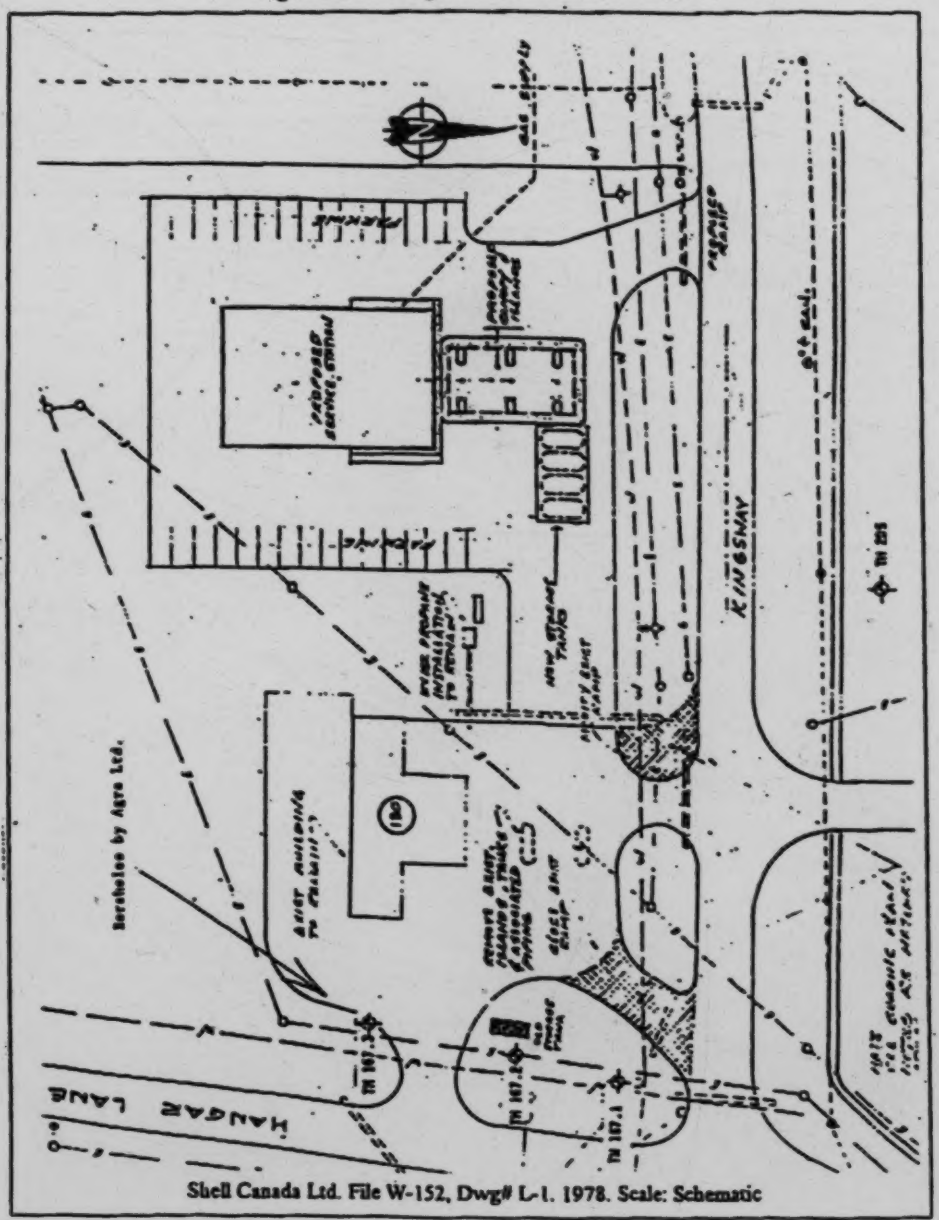

N
MW-CF5
MW-91099
KINGSWAY
MW-971
MW-972
MW-G
MW-F
MW-H
MW-973
MW-91095
AH-13
AH-12
AH-20
AH-11
AH-15
MW-976
MW-14A
MW-C
MW-B
MW-A
AH-22
MW-1673
AH-10
AH-10A
HANGAR LANE
MW-CF2
MW-91091
MW-CF3
LEGEND
Monitoring Well Location
Auger Hole Location
Buried Water Line
Buried Sewer Line and Manhole
30 m
4 WING COLD LAKE
OLD IMPERIAL
FIGURE 35

Figure 36: Original Gas Station Layout, 1978



Shell Canada Ltd. File W-152, Dwg# L-1. 1978. Scale: Schematic

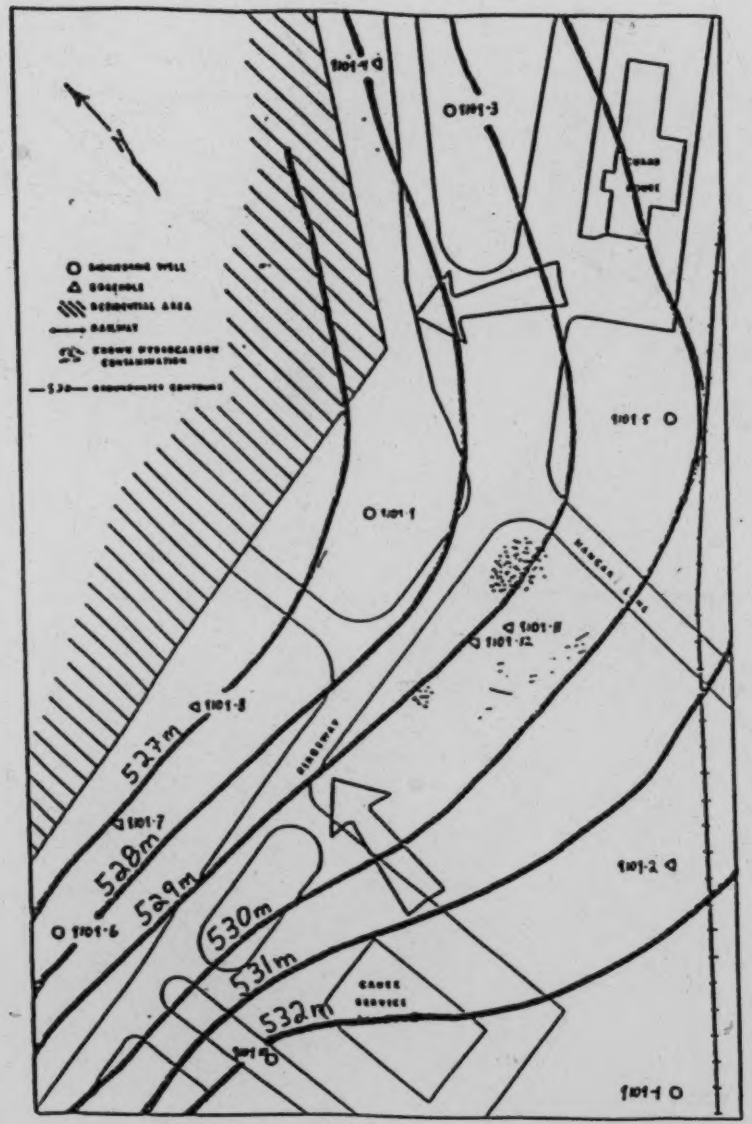


Figure 37: Boreholes & Groundwater Contours (Custom Environmental)

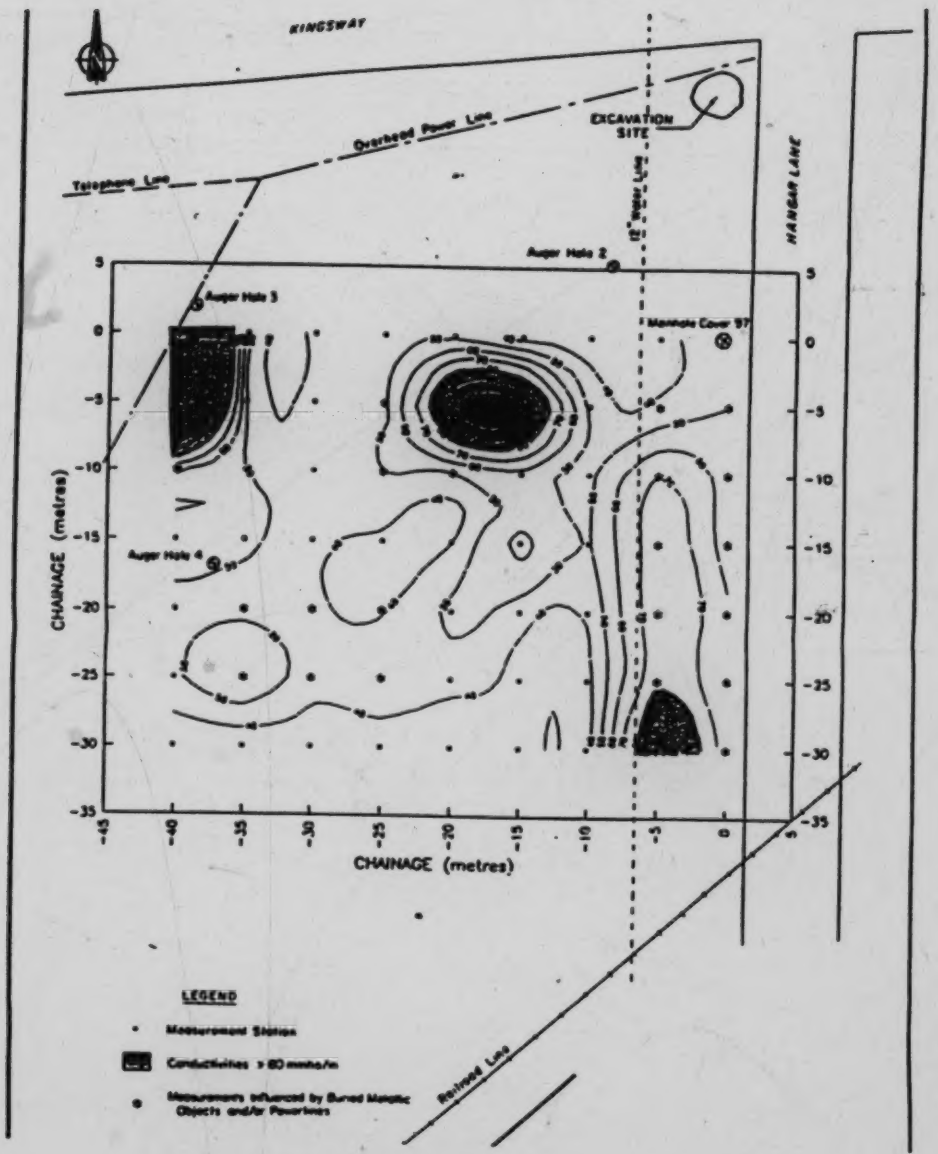


Figure 38: Geophysics Conductivity Contour Map (EM 31 VG)
(Geo-Physi-Con, 1991)

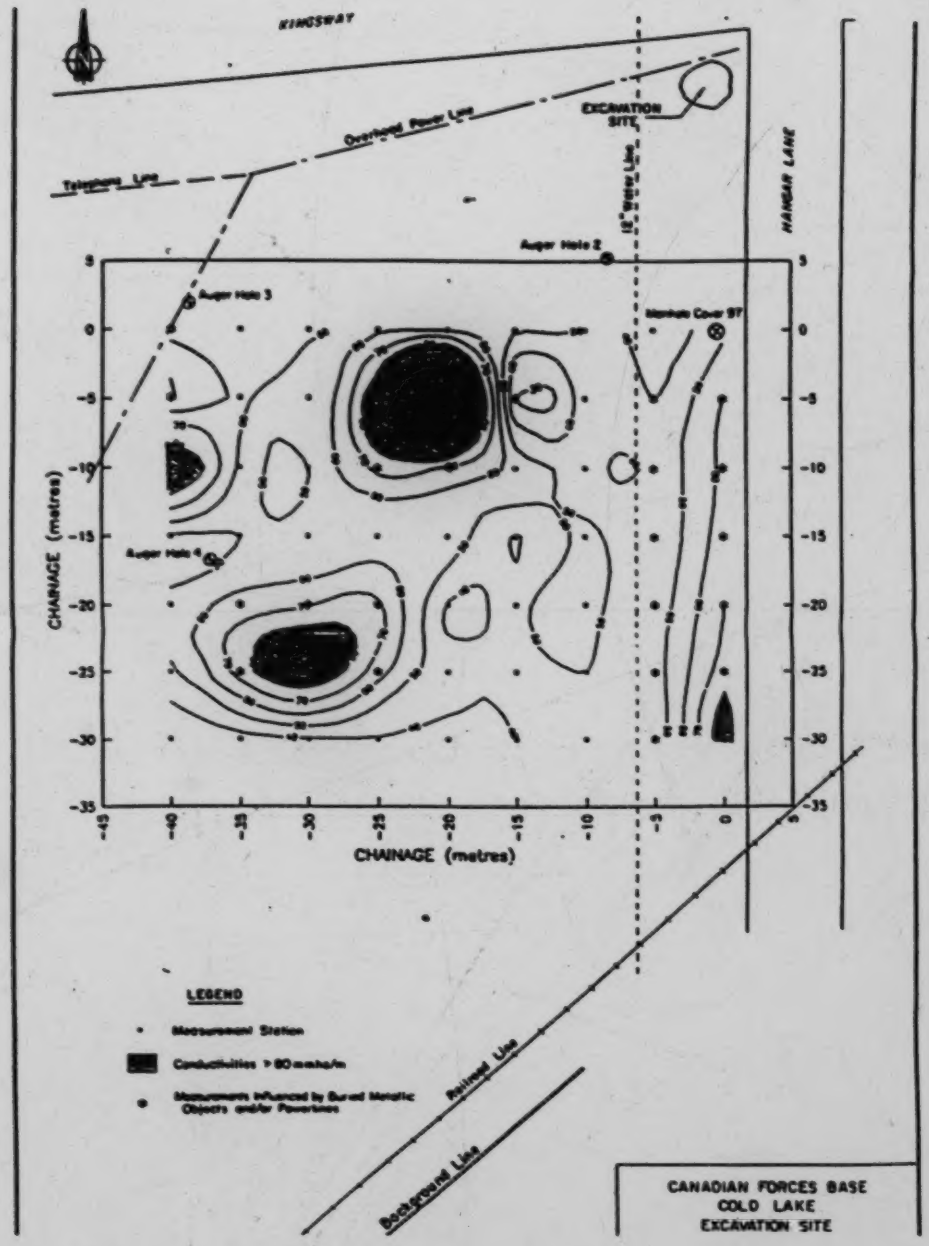
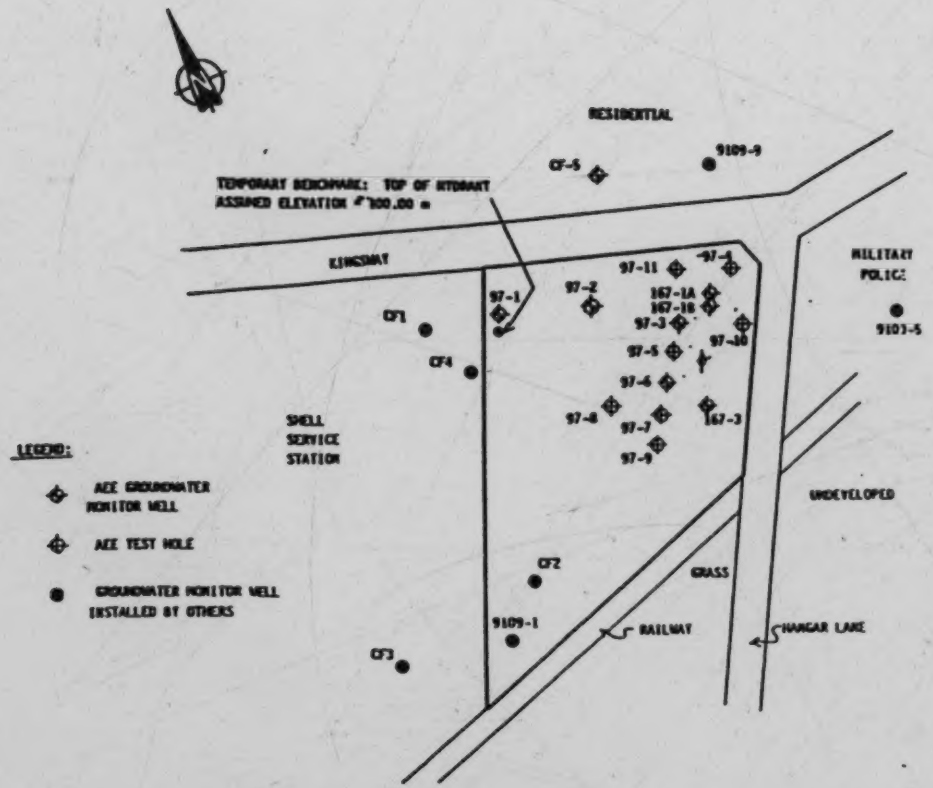


Figure 39: Geophysics Conductivity Contour Map (EM 31 HZ)
(Geo-Phvsi-Con. 1991)

Figure 40: HBT Agra Monitoring Wells, 1993



SITE PLAN SHOWING LOCATION OF TEST HOLES AND GROUNDWATER MONITOR WELLS.

PLAN SCALE 1:1250

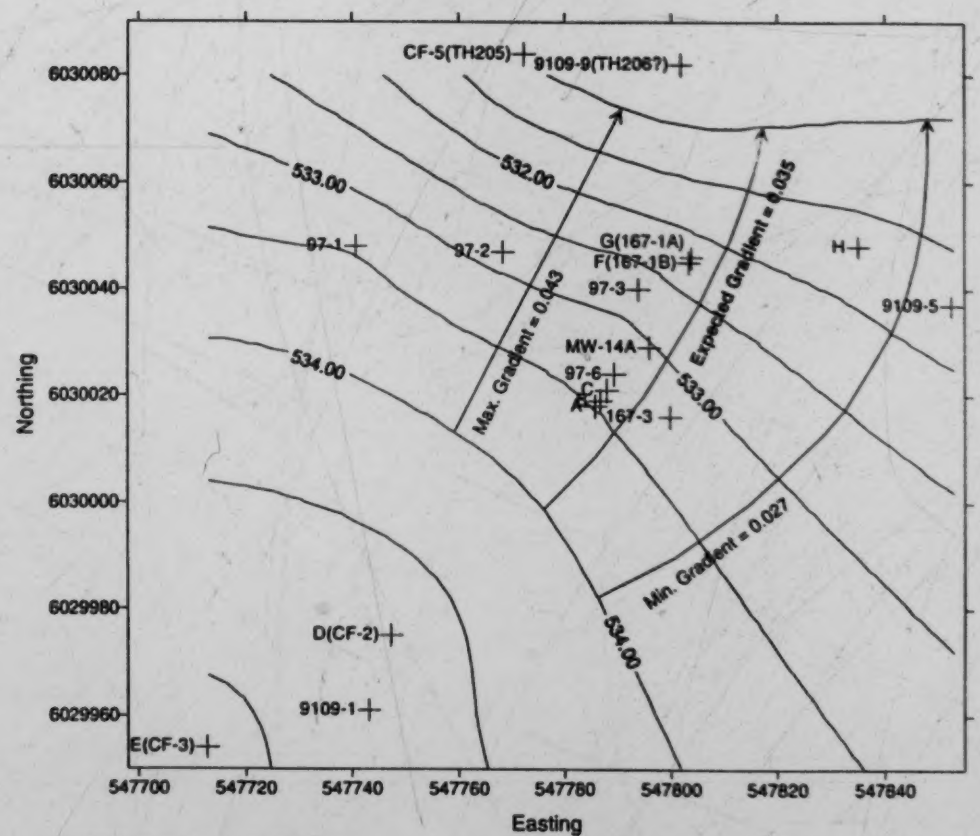
DETAILS ARE APPROXIMATE ONLY. THIS FIGURE IS NOT INTENDED FOR DESIGN OR CONSTRUCTION PURPOSES.

Figure 41: Agra E&E Monitoring Wells, 1997

Figure 42 Old Imperial Site

Water Table Elevation

JUNE 1998 (m elevation)



NOTE: Water levels obtained from:

CF-3 (E)	F(167-1B)
9109-1	G(167-1A)
CF-2 (D)	CF-5
A	9109-9
B	H
C	9109-5
97-6	97-1
97-3	97-2

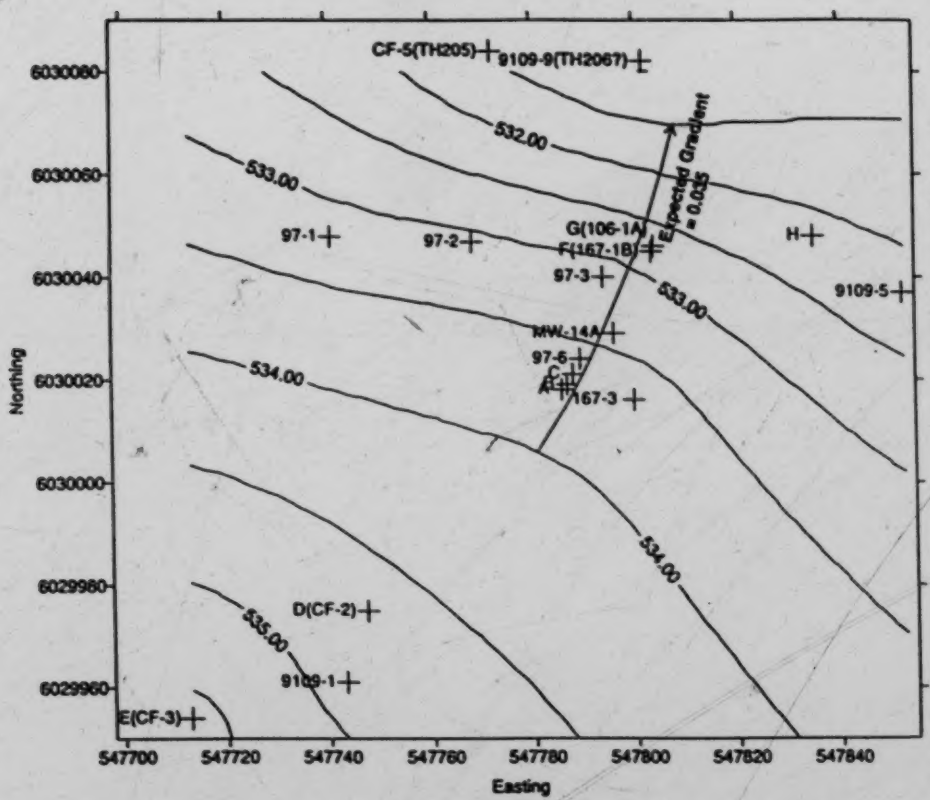
SCALE (m)

0.00 20.00 40.00 60.00 80.00

Figure 43 Old Imperial Site

Water Table Elevation

AUGUST 1998 (m elevation)



Note: water levels obtained from:

CF-3 (E)	97-2
9109-1	G(167-1A)
97-5	CF-5
A	9109-9
B	H
C	9109-5
97-3	

Scale (m)

0.00 20.00 40.00 60.00 80.00

Figure 44 Old Imperial Site

Water Table Elevation

OCTOBER 1998 (m elevation)

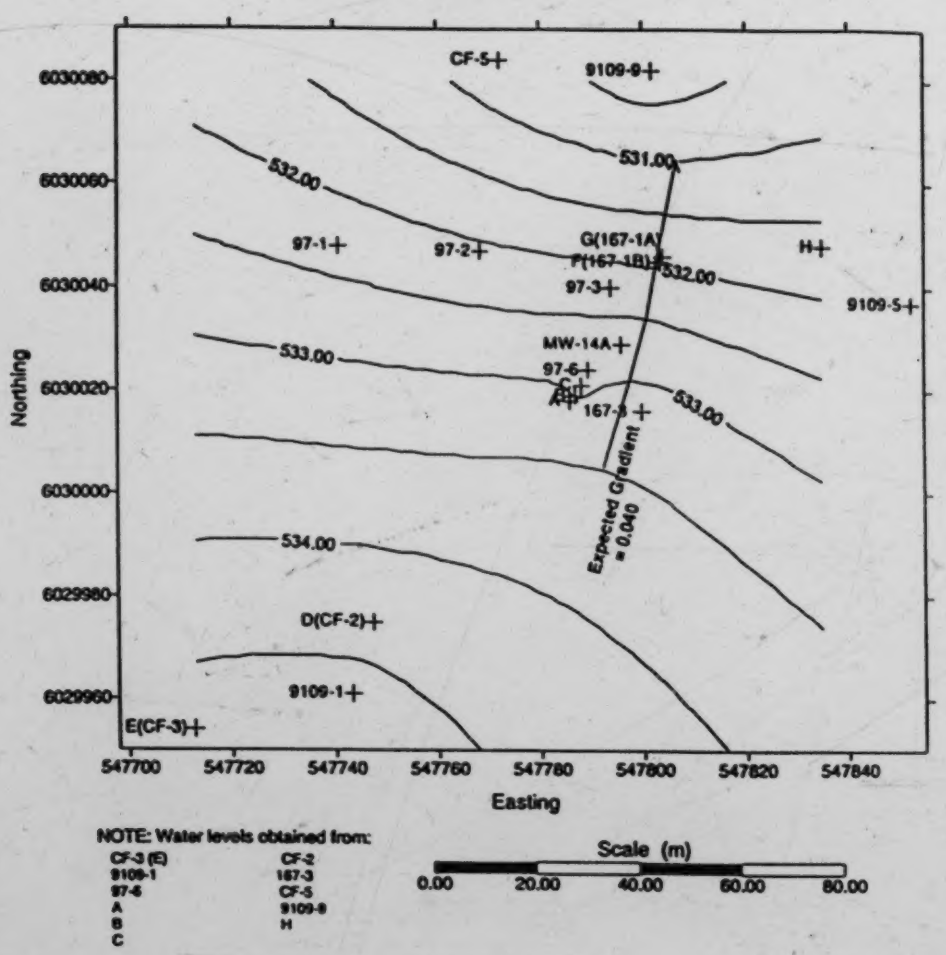


Figure 45: Old Imperial Site

ESTIMATED EXTENT OF SOIL CONTAMINATION
2.5-4.0m

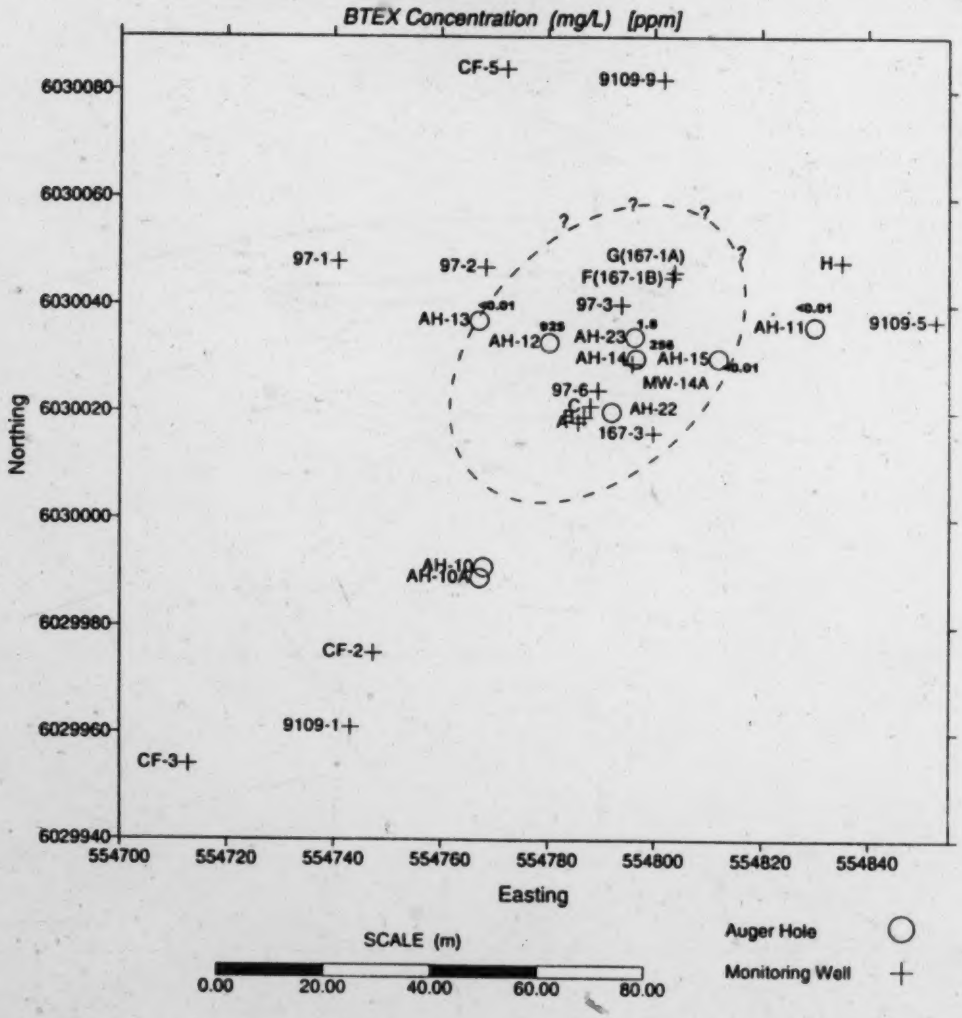


Figure 46: Old Imperial Site

ESTIMATED EXTENT OF GROUNDWATER CONTAMINATION

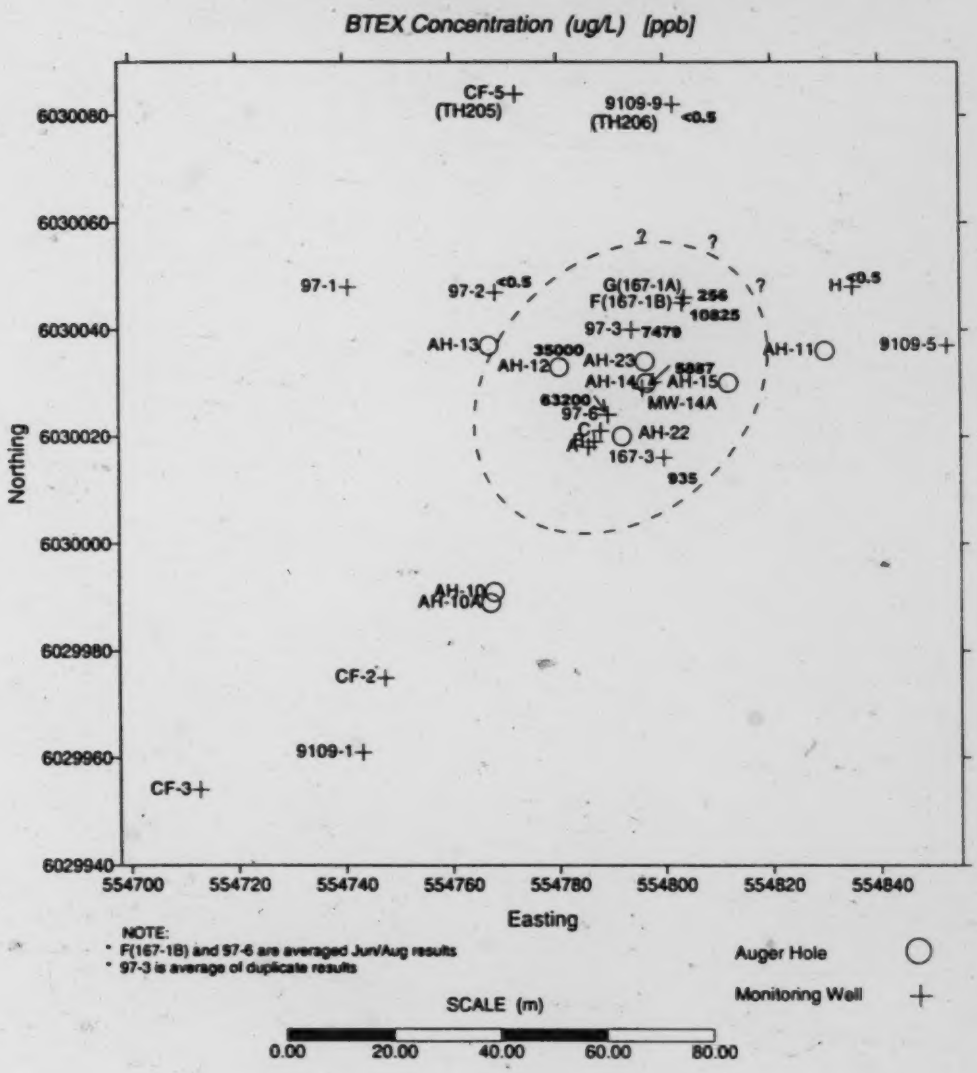
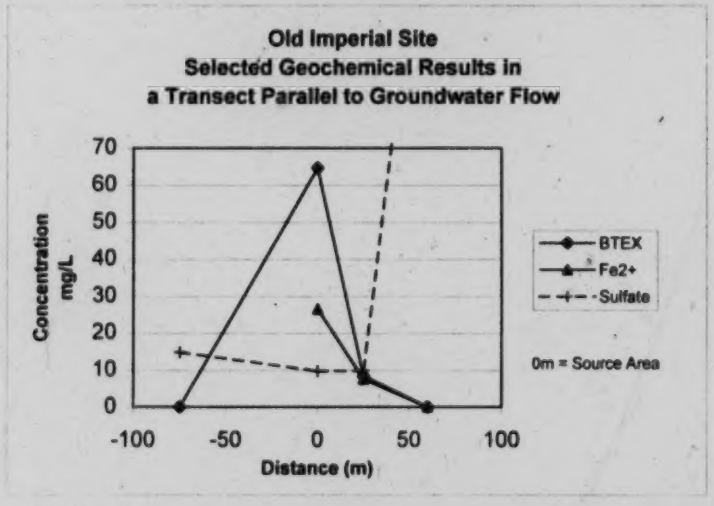
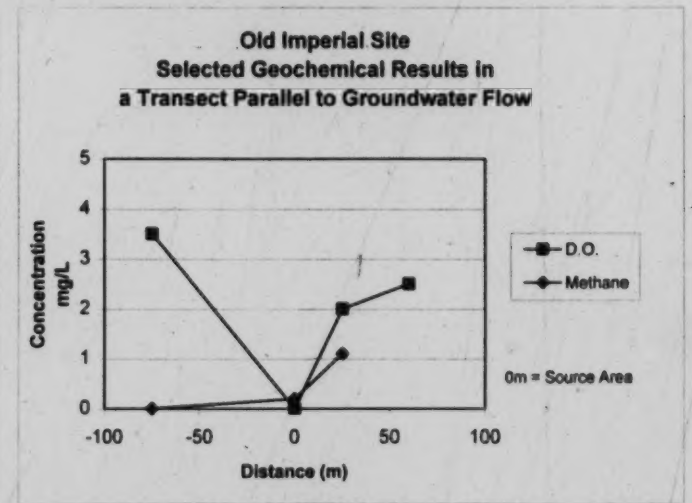


Figure 47: Selected Geochemical Results at the Old Imperial Site

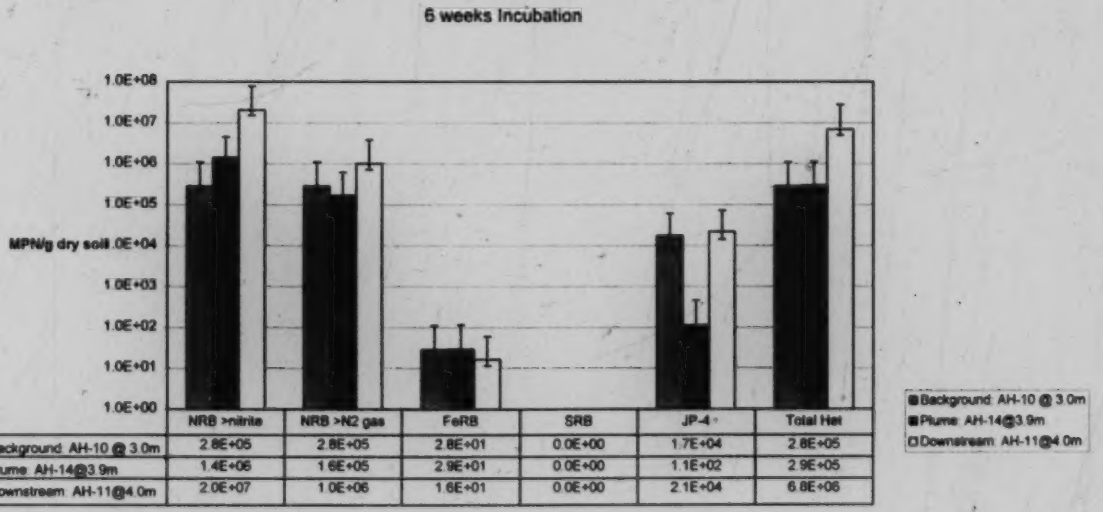




Location	Monitoring Well	Distance m	BTEX mg/L	D.O. mg/L	Nitrate mg/L	Sulfate mg/L	Sulfide mg/L	Fe^{2+} mg/L	Methane mg/L
upgradient	9109-1	-75	0	3.5	0	14.8	0	NA*	0
near source	97-6	0	64.6	0	0	9.7	0.02	26.5	0.2
downgradient	F (167-1)	25	8.3	2	0	9.8	0.004	7.5	1.1
far downgradient	9109-9	60	0	2.5	0	150	0	0	NA

*NA : Not Analyzed

Figure 48: OIS Microbial Enumeration



	NRB >nitrite	NRB >N2 gas	FeRB	SRB	JP-4	Total Het
Background AH-10 @ 3.0m	2.8E+05	2.8E+05	2.8E+01	0.0E+00	1.7E+04	2.8E+05
Plume AH-14@3.9m	1.4E+06	1.6E+05	2.9E+01	0.0E+00	1.1E+02	2.9E+05
Downstream AH-11@4.0m	2.0E+07	1.0E+06	1.6E+01	0.0E+00	2.1E+04	6.8E+06

NRB>nitrite = Nitrate reducing bacteria that converted nitrate to nitrite
NRB>N2 gas = Nitrate reducing bacteria that converted nitrate to nitrogen gas
FeRB = Iron reducing bacteria
SRB = Sulfate reducing bacteria
JP-4 = JP-4 degrading bacteria
Total Het = Total Heterotrophic bacteria

Figure 49: OIS Microbial Activity

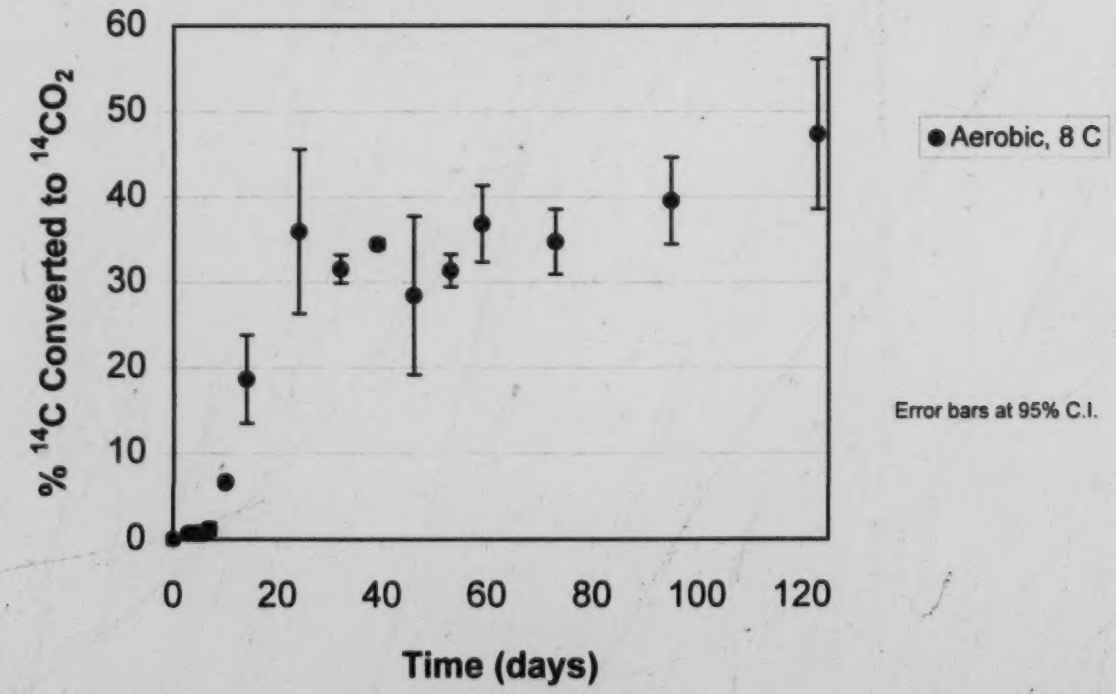


Figure 50: OIS First Order Biodegradation Rate

Sample Conditions: Aerobic 8°C

Assume 50% Conversion to $^{14}CO_2$

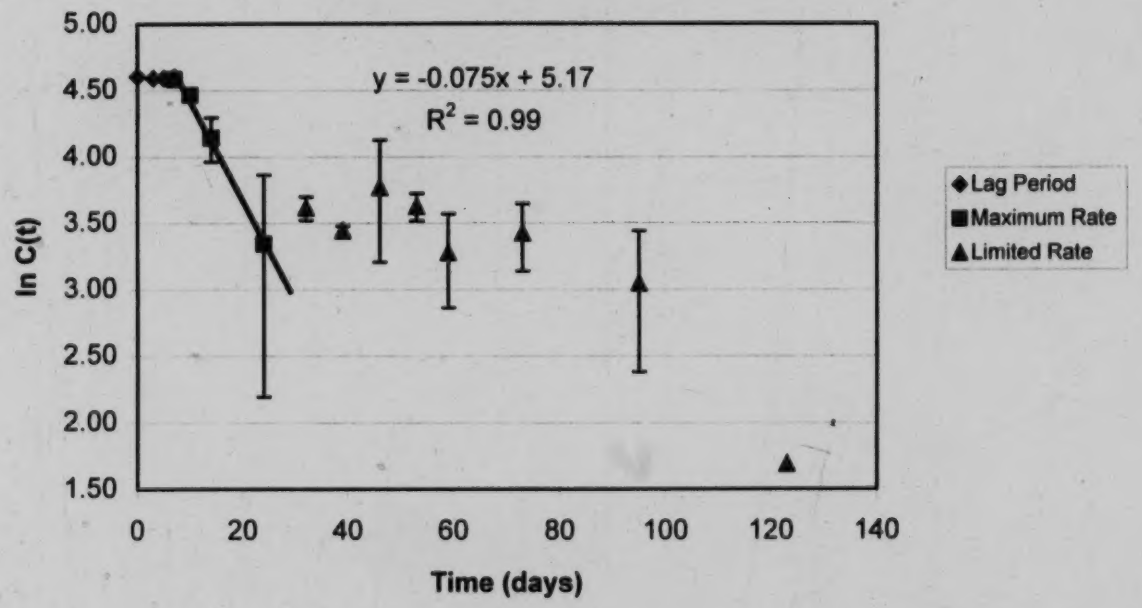


Figure 51: OIS First Order Biodegradation Rate

Sample Conditions: Aerobic 8°C

Assume 68% Conversion to $^{14}CO_2$

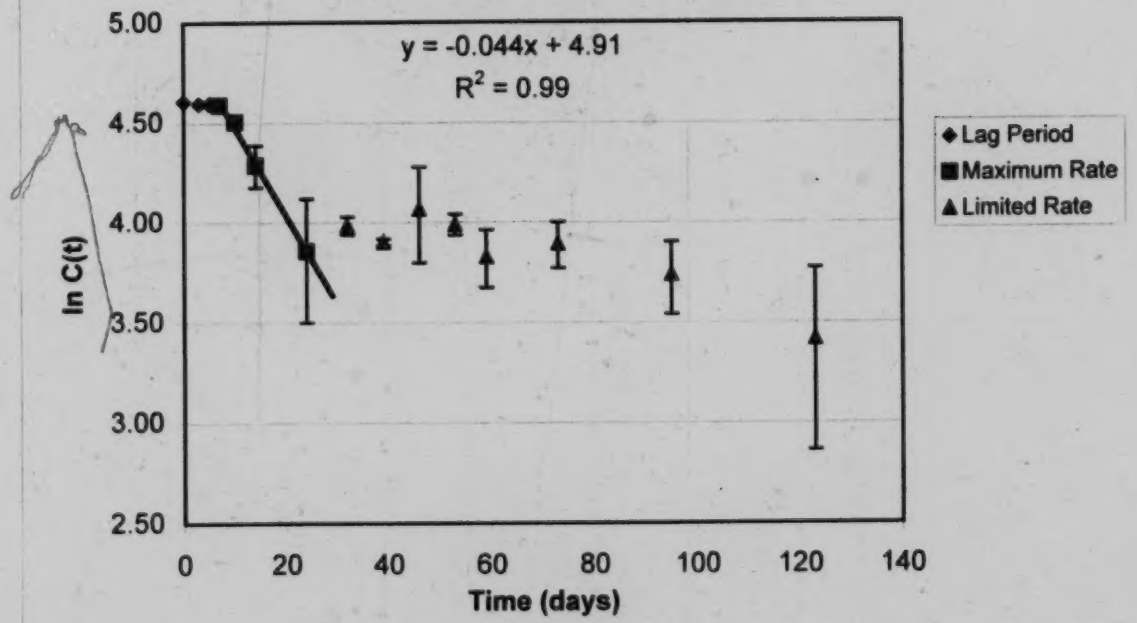


Figure 52: Declining Growth Model
Old Imperial 8 C

$C(t) = C_{max}(1-e^{-kt})$

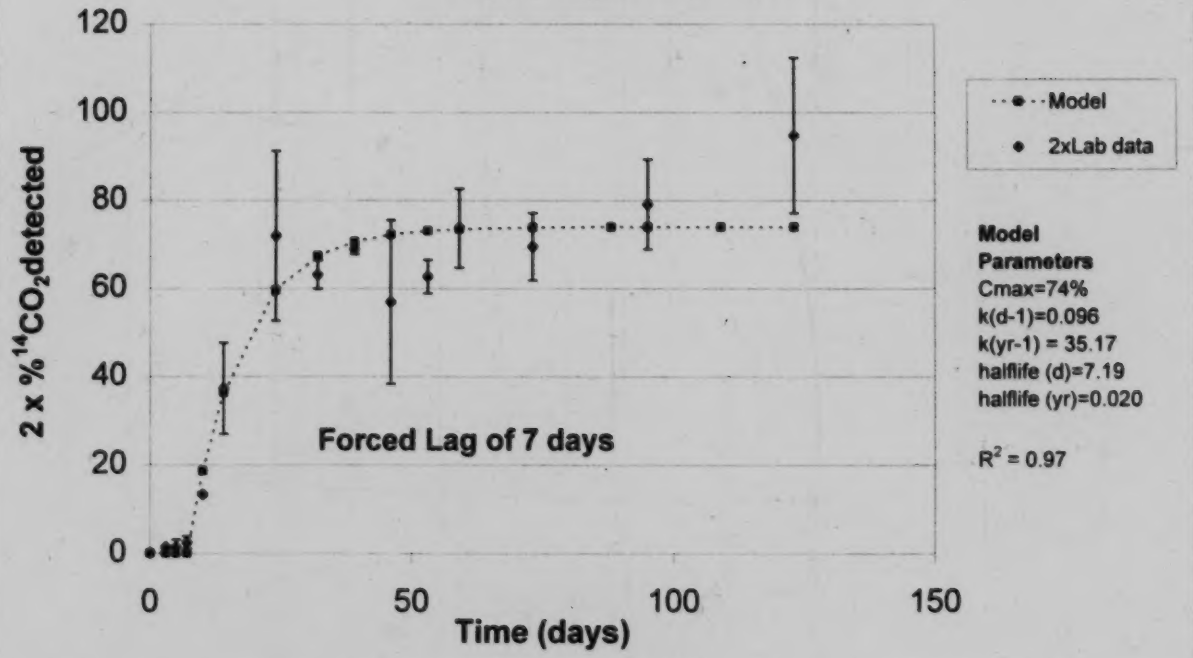
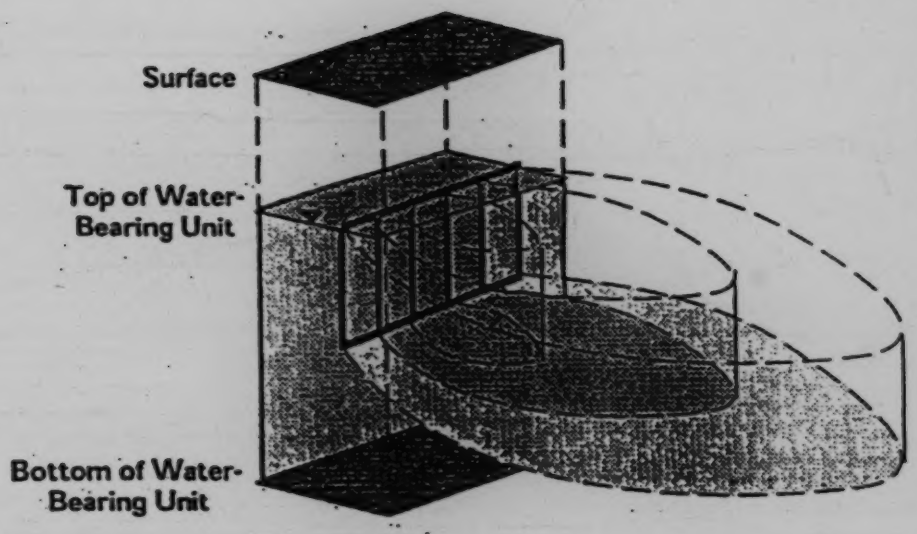


Figure 53: BIOSCREEN Source Distribution Diagram



From Newell et al., 1997

Figure 54A: Scenario A, Calibrated Model Input Data

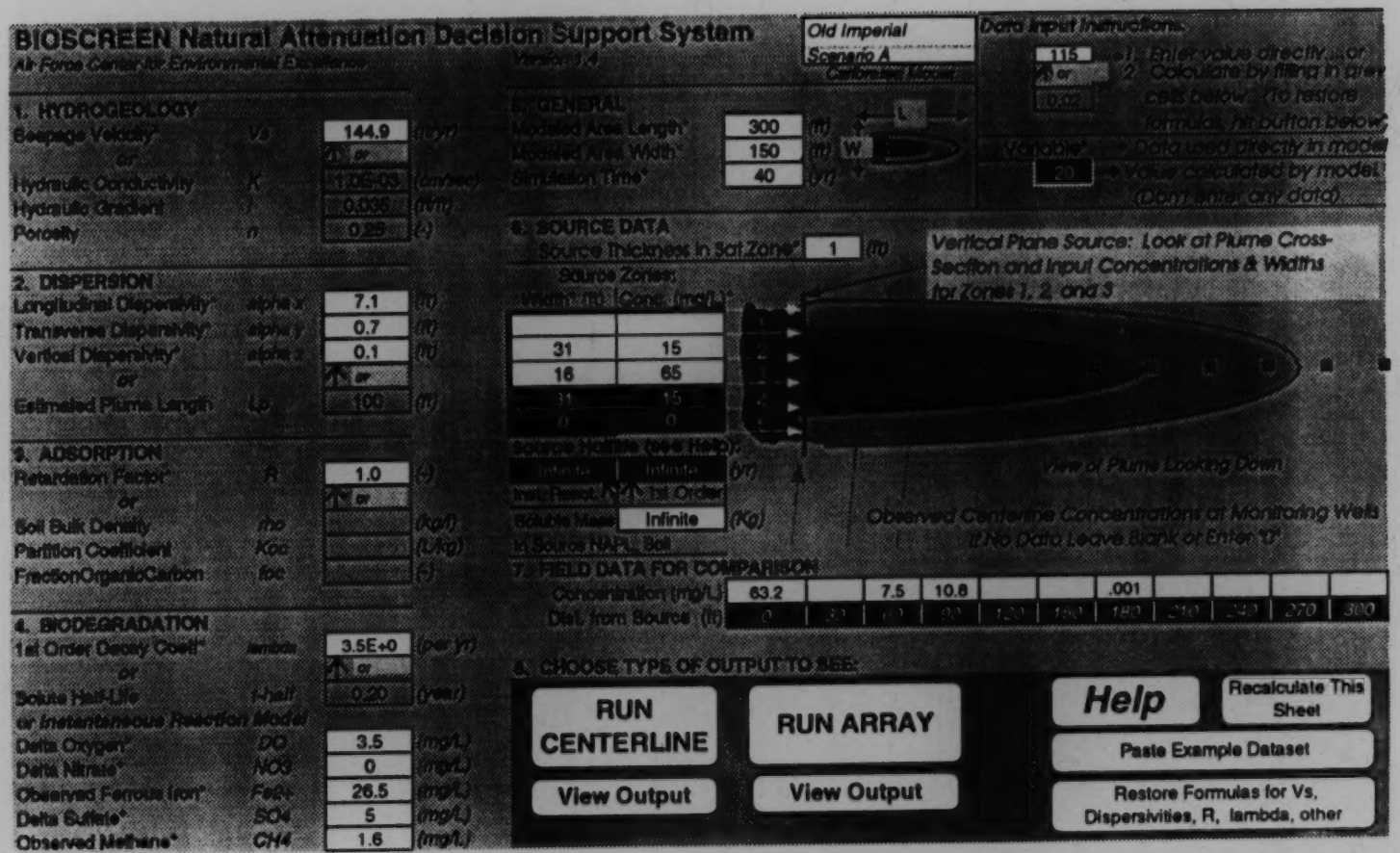


Figure 54B: Scenario A, Calibrated Model

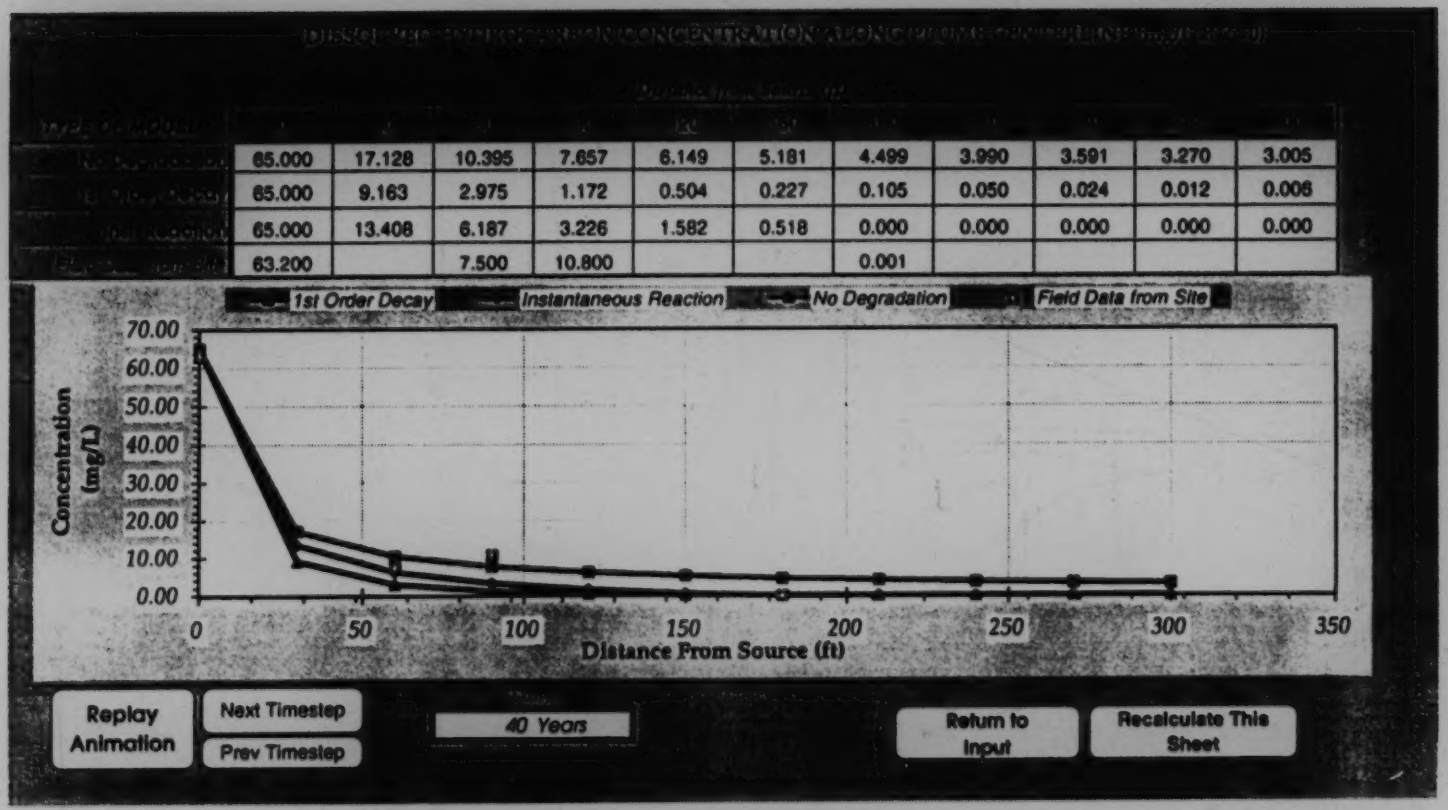


Figure 55A: Scenario B Calibrated Model Input Data

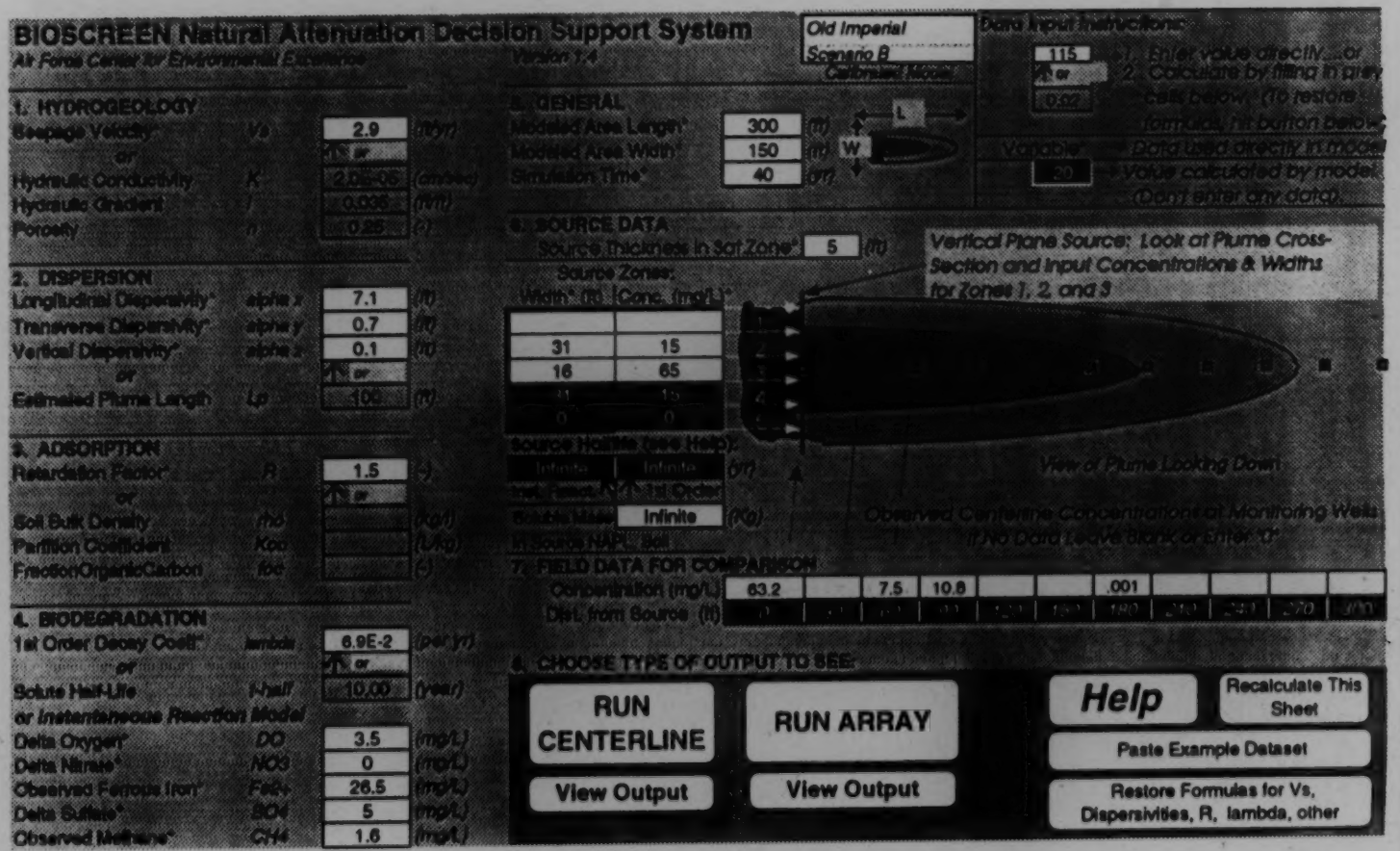
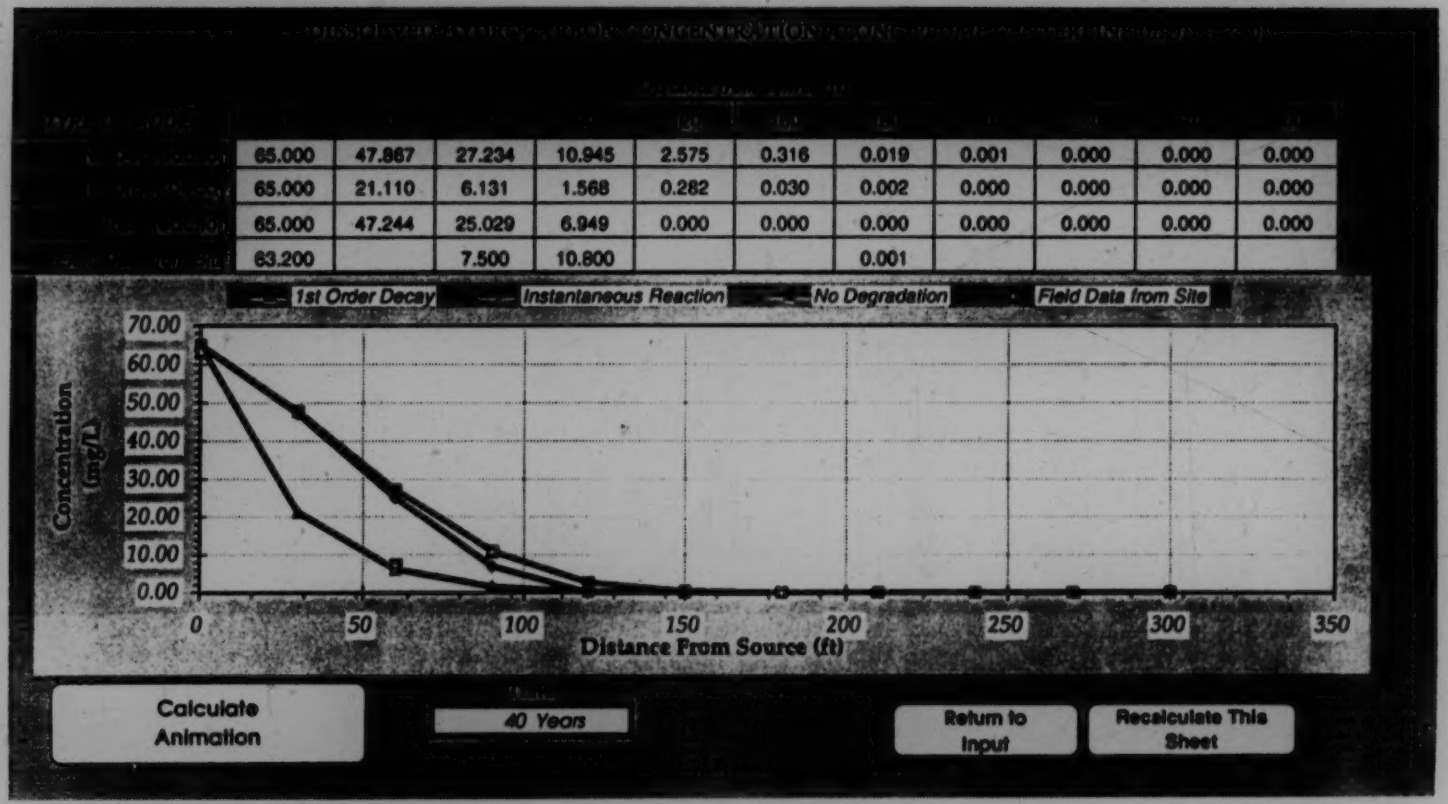


Figure 55B: Scenario B, Calibrated Model



65.000	47.867	27.234	10.945	2.575	0.316	0.019	0.001	0.000	0.000	0.000
65.000	21.110	6.131	1.568	0.282	0.030	0.002	0.000	0.000	0.000	0.000
65.000	47.244	25.029	6.949	0.000	0.000	0.000	0.000	0.000	0.000	0.000
63.200		7.500	10.800			0.001				

Figure 56: Scenario A, Model Prediction at Time = 140 yrs (100 years into the future)

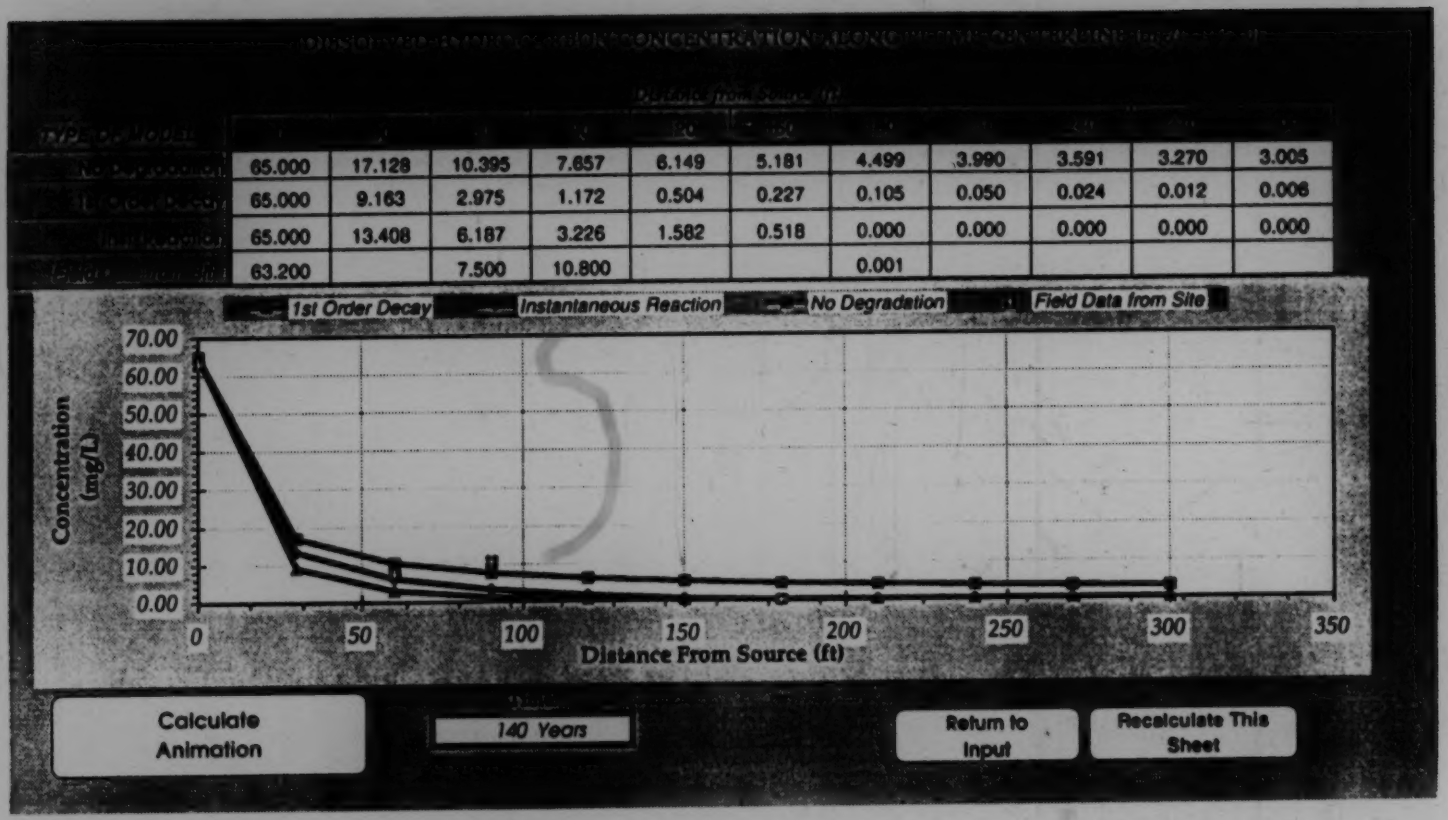


Figure 57: Scenario B, Model Prediction at Time =140 yrs (100 years into the future)

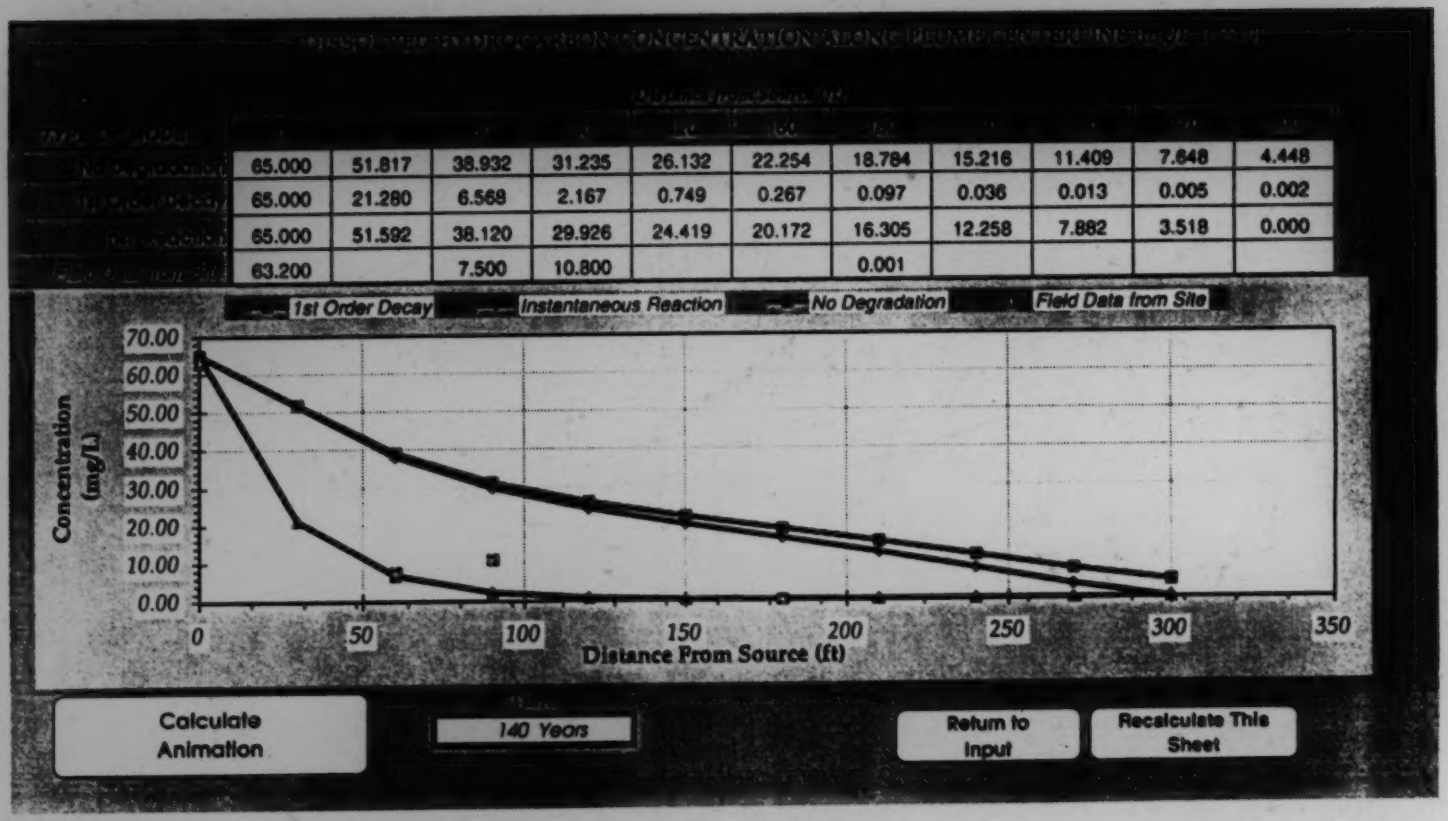


Figure 58: Scenario A, Model Prediction at Time = 140 yrs with Source half-life = 100 yrs

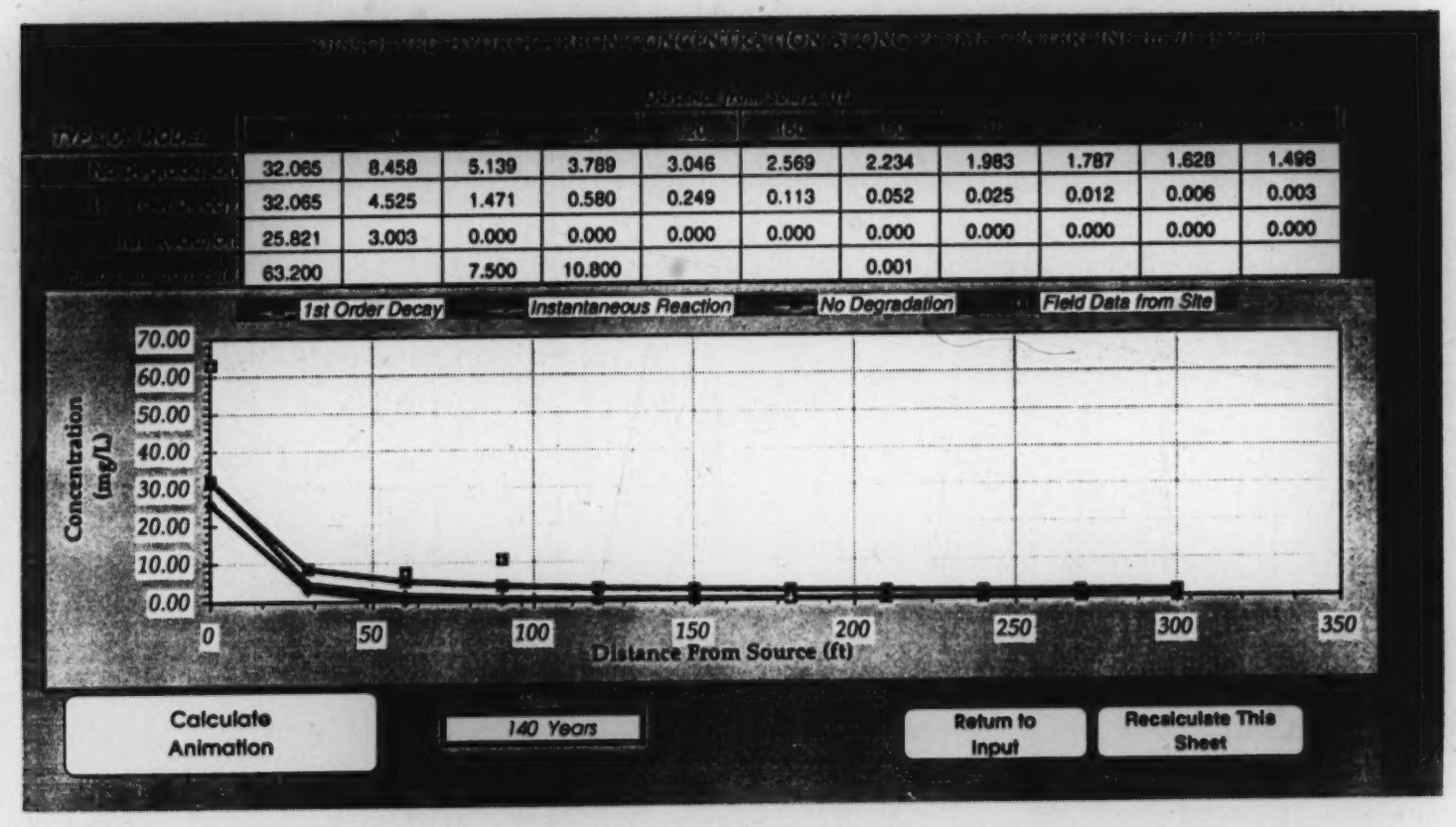
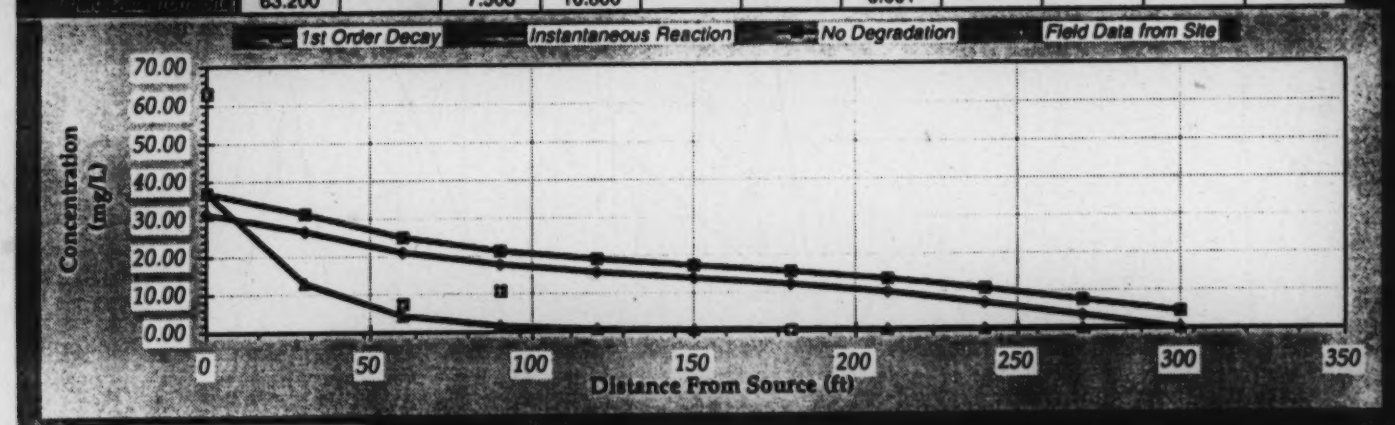


Figure 59: Scenario B, Model Prediction at Time =140 yrs with Source half-life = 100 yrs

	36.933	31.348	25.078	21.421	19.082	17.302	15.550	13.411	10.707	7.841	4.448
	36.933	12.874	4.230	1.486	0.547	0.207	0.080	0.032	0.012	0.005	0.002
	31.322	26.735	21.091	17.751	15.604	13.938	12.209	9.960	6.983	3.510	0.000
	63.200		7.500	10.800			0.001				



Calculate Animation | 140 Years | Return to Input | Recalculate This Sheet

6 MICROCOSM EXPERIMENT DISCUSSION

Toluene has been shown to be the most rapidly utilized of BTEX compounds in microcosm studies (Phelps and Young, 1999), which was the main reason for using it for this experiment. Caution must therefore be exercised when applying the interpreted laboratory reaction rate to the field site as the other more slowly degraded components of BTEX will likely take longer to degrade. Other reasons for slower observed field biodegradation rates as compared to laboratory rates (Wiedemeier et al., 1995) include the preferential degradation of other organic compounds rather than toluene, site heterogeneity, and potentially toxic effects on the microbial community due to locally high concentrations of hydrocarbons.

The FFTA site contamination is primarily the result of JP-4 jet fuel leakage into the aquifer, while the Old Imperial site contamination is expected to be due to gasoline hydrocarbons. Gasoline contains a much higher fraction of BTEX than JP-4 (Table 1), however BTEX are still the most soluble components in both mixtures and therefore constitute the bulk of the dissolved contaminant plume at both sites.

The laboratory experiment conducted in this research program allows comparison of toluene biodegradation at different temperatures and in different soil types. The following sections review general trends in the experimental data and the influence of temperature on the biodegradation of toluene.

6.1 General Trends in Microcosm Experimental Data

Trends in the data, particularly with respect to the lag period, the extent of mineralization, and the rate constant can be compared to examine the influence of temperature, soil type, and the addition of nutrients on biodegradation.

The shortest lag time, the highest biodegradation rate and the highest percent conversion of toluene to CO_2 was observed in the aerobic microcosms incubated at 22°C. This observation indicates that this was the optimal environment for microbial growth of the conditions tested. The slowest rate and the lowest percent conversion of toluene to CO_2 was observed in the anaerobic

microcosms incubated at 8°C. This suggests that these conditions were the least optimum for microbial growth of those tested in this experiment.

The Old Imperial and FFTA samples incubated at 8°C exhibited a similar rate and extent of toluene mineralization. This suggests that the soil type (clay till and glaciofluvial sand) did not appear to influence the lag time, the rate, or the extent of biodegradation. This is surprising, as the slightly higher soil organic content in the Old Imperial soil might have been expected to cause greater sorption of toluene to the soil. This in turn might reduce the bioavailability of toluene and prevent its conversion to CO_2. An explanation for why this did not occur may be that the available adsorption sites within the Old Imperial soil might have already been occupied since the site has been contaminated for many years.

The nitrogen and phosphorus amended controls did not appear to enhance biodegradation at either site. While it is possible that the supplied dose was not adequate to cause a measurable effect, it may indicate that the environment for microbial growth was not nutrient limited.

The amount of radioactivity in the first liquid scintillation vial can be interpreted as the amount of ^{14}C-toluene that was flushed out of a serum bottle and trapped in the scintillation fluor. Inspection of the percent toluene recovered during each flushing trial (Appendix H) indicates that in general, a smaller amount of ^{14}C-toluene was recovered in the first trapping vial in the Old Imperial samples than the FFTA samples. This may be due to less effective sparging of ^{14}C-toluene out of the Old Imperial clayey silt soil and may or may not reflect on the amount of $^{14}CO_2$ which was sparged from the sample. CO_2 would have more readily partitioned to the vapour phase than toluene.

6.2 Influence of Cold Temperature on Microbial Activity

This section will examine the relationships between the lag time, the extent of mineralization, and the reaction rates for the microcosm study samples. These relationships can be used to infer the influence of temperature on the biodegradation of hydrocarbons.

6.2.1 Lag Time

Lag times observed in microcosm experiments are due primarily to the time interval required for microorganisms to adapt to different environmental conditions. The length of the lag period can indicate how well adapted the microorganisms are to the geochemical environment and the level of contaminant concentration in the microcosm (Anderson and Lovley, 1999). Corseuil and Weber (1994) suggest that the delay in the onset of measurable microbial activity exhibited in contaminant mineralization is due to the time required to develop a sufficiently high biomass concentration. They observed lags of 2-3 days for xylenes and benzene and 4.5 days for toluene in a column experiment (Corseuil and Weber, 1994). Other workers have determined the lag for toluene mineralization to vary between 1-4 days in liquid batch-type experiments carried out at room temperature (Kelly et al., 1996; Zhang and Bouwer, 1997).

The lag times observed in this study (summarized below) are slightly longer than those observed in selected other studies, indicating that the indigenous microorganisms appeared to be moderately affected by the environment in the microcosm. The lag may be due to the adjustment of the microbial population from the dominantly anaerobic conditions at the sample location to the aerobic conditions in the microcosm. This may account for the lack of obvious lag period in the anaerobic microcosms, but the resolution of the data is not adequate to conclude this with certainty. At 22°C the lag time was approximately 5 days while at 8°C both samples exhibited a lag of approximately 7 days. The difference between the lag times at different temperatures may indicate that the optimal conditions for the growth of indigenous microorganisms are closer to 22°C than to 8°C.

Estimated Experimental Lag Time with the Declining Growth Model

Sample	Lag Time (days)
FFTA Aerobic 8°C	7
FFTA Aerobic 22°C	5
OIS Aerobic 8°C	7

6.2.2 Extent of Mineralization

The influence of temperature on reaction equilibrium is introduced in Section 2.2.1. Results from this experiment (summarized below) indicate that at 22°C the mineralization of toluene in microcosm experiments may be more complete than at 8°C. At 22°C, 100% of the ^{14}C toluene is expected to be mineralized based on the Declining Growth Model prediction, while at 8°C only approximately 80% of the toluene may be mineralized. The declining mineralization rate and resulting model prediction of incomplete mineralization (C_{max} <100%) may be due to the change in microbial population to dominantly facultative or anaerobic microbes as it can be expected that there was decreasingly available DO in the microcosms with time. This does not explain the difference between the model predictions at 8°and at 22°C, however. If the lower extent of mineralization exhibited by these samples is related to the incubation temperature difference, then it may be presumed that at cold temperature contaminated sites, low levels of residual organic contamination may be difficult to biodegrade.

Predicted Extent of Mineralization by Declining Growth Model

Sample	C_{max} (% $^{14}CO_2/^{14}C_T$)
FFTA Aerobic 8°C	83
FFTA Aerobic 22°C	107
OIS Aerobic 8°C	74

6.2.3 Rate Constant

As discussed in Section 2.2.2, the constant θ has been used to compare the rate of reactions at different temperatures. The traditional expectation for biologically mediated reactions is that the reaction rate will double for every 10°C increase in temperature. For this relationship, the constant θ can be calculated by rearranging Equation 12:

$$\theta = \sqrt[(T1-T2)]{\frac{k_{T1}}{k_{T2}}} \qquad [30]$$

$$\theta = \sqrt[10]{2}$$

$$= 1.072$$

Experimental Rate Constants

Experimental Conditions	First Order Rate Constant, k (day^{-1})
FFTA Aerobic 8°C	0.038
FFTA Aerobic 22°C	0.068
OIS Aerobic, 8°C	0.044 *

*Calculated by assuming 68% of toluene converted to $^{14}CO_2$ (same as FFTA samples)

By Equation 30, the value for θ can be derived using the FFTA first order rate constants for the FFTA sample (shown above):

$$\theta = \sqrt[14]{\frac{0.07}{0.04}}$$

$\theta = 1.041$

The constant can be calculated in the same manner with the Declining Growth rate constants for the FFTA samples to be 1.046. The experimentally determined values for θ are quite similar to that calculated for a doubling of reaction rate with a 10°C change in temperature (1.072). They also fall within the range of values for the constant observed for other biologically mediated reactions (Table 4).

The measured rate is slightly faster than predicted by the traditional temperature kinetic relationship, but given that the rate estimates are only order of magnitude, they are not different by a statistically significant margin. These results support the accepted understanding that the rate of bioremediation approximately doubles for a 10°C change in temperature.

7 UNRESOLVED QUESTIONS/FURTHER WORK

Further research will be required to resolve some of the interesting questions raised in the course of this work. The limitations of the experimental design of the rate study may have reduced the accuracy of the results somewhat. Additional site characterization, while not necessary to complete the intrinsic bioremediation assessment, could further refine the site conceptual model.

7.1 Experimental Limitations

Some difficulty was encountered attempting to provide a consistent slurry (soil: groundwater ratio) to each vial in the microcosm study. More refined laboratory techniques to deliver the soil and water with greater accuracy, while still limiting volatilization, may reduce experimental error and refine estimates of the model parameters. Measurement of TEA and degradation products in the microcosms (incl. DO, NO_2^-/NO_3^-, Fe^{2+}, SO_4^{2-}, and CH_4) would have provided more supporting evidence of biodegradation, indicated the dominant anaerobic TEAP, and permitted a stoichiometric balance of TEAs reduced to toluene degraded. The use of a colourimetric redox indicator in the vials could qualitatively show when dissolved oxygen is depleted in the aerobic trials. Experimental trials of samples incubated at a wider range of temperatures could better define the constant θ for biodegradation.

7.2 Additional Site Characterization

More precise delineation of TEAP zones, perhaps via dissolved H_2 gas analysis, could refine each site conceptual model considerably (Vroblesky and Chapelle, 1994). If this analysis was repeated over time, then the temporal and spatial variation of contamination concentrations and TEAPs could be investigated. A detailed hydrogeological investigation of the groundwater flow at each site could improve the understanding of the mechanisms for contaminant migration. At the FFTA in particular, the source and extent of the conductive anomaly has not been verified. Additional monitoring well installations or HydroPunch® measurements to better define vertical

head variations could provide the data necessary to assemble a meaningful 3-dimensional contaminant flow model. It has been suggested that in the upper 10m of the ground, diurnal and seasonal variations in air temperature can create a zone that is thermally transient (Freeze and Cherry, 1979). Accurate groundwater temperature measurements at each site, over the entire year and perhaps with greater attention to vertical differences, may provide interesting results which refine the site model. Measurement of the biodegradation rate in the field by calibration with a conservative tracer could relate field and laboratory measurements of biodegradation. This work may help refine the current understanding of bioremediation of hydrocarbons and, in particular, may assist in resolving the conflicting MPN and geochemical evidence for nitrate and sulfate reduction at the sites.

8 CONCLUSIONS

Intrinsic bioremediation is occurring at each site based on 3 lines of evidence:

- Limited contaminant migration despite long term contamination (>40 years)
- Geochemical indicators of TEAPs
- Direct microbiological evidence via enumeration of hydrocarbon degrading microorganisms and microcosm studies demonstrating toluene biodegradation with indigenous microbes

Intrinsic bioremediation appears to be ongoing at the colder temperatures at both Cold Lake, AB sites.

Intrinsic bioremediation appears to be a viable remedial approach at the FFTA site because the capacity for biodegradation appears adequate for the low aqueous concentration of BTEX at the site.

Intrinsic bioremediation is not likely a viable remedial alternative by itself at the Old Imperial site due to the high concentration of dissolved BTEX near the source area and the risk of contaminants intercepting the drinking water lines at the site. Additional source removal is recommended and intrinsic bioremediation should be used as a final remedial stage.

The rate of biodegradation in the microcosm study at 8°C appears to be slightly less than half that at 22°C as interpreted by both simple and modified first order kinetics.

In the microcosm experiment, the extent of biodegradation of toluene appears to be approximately 20% greater at 22°C than at 8°C.

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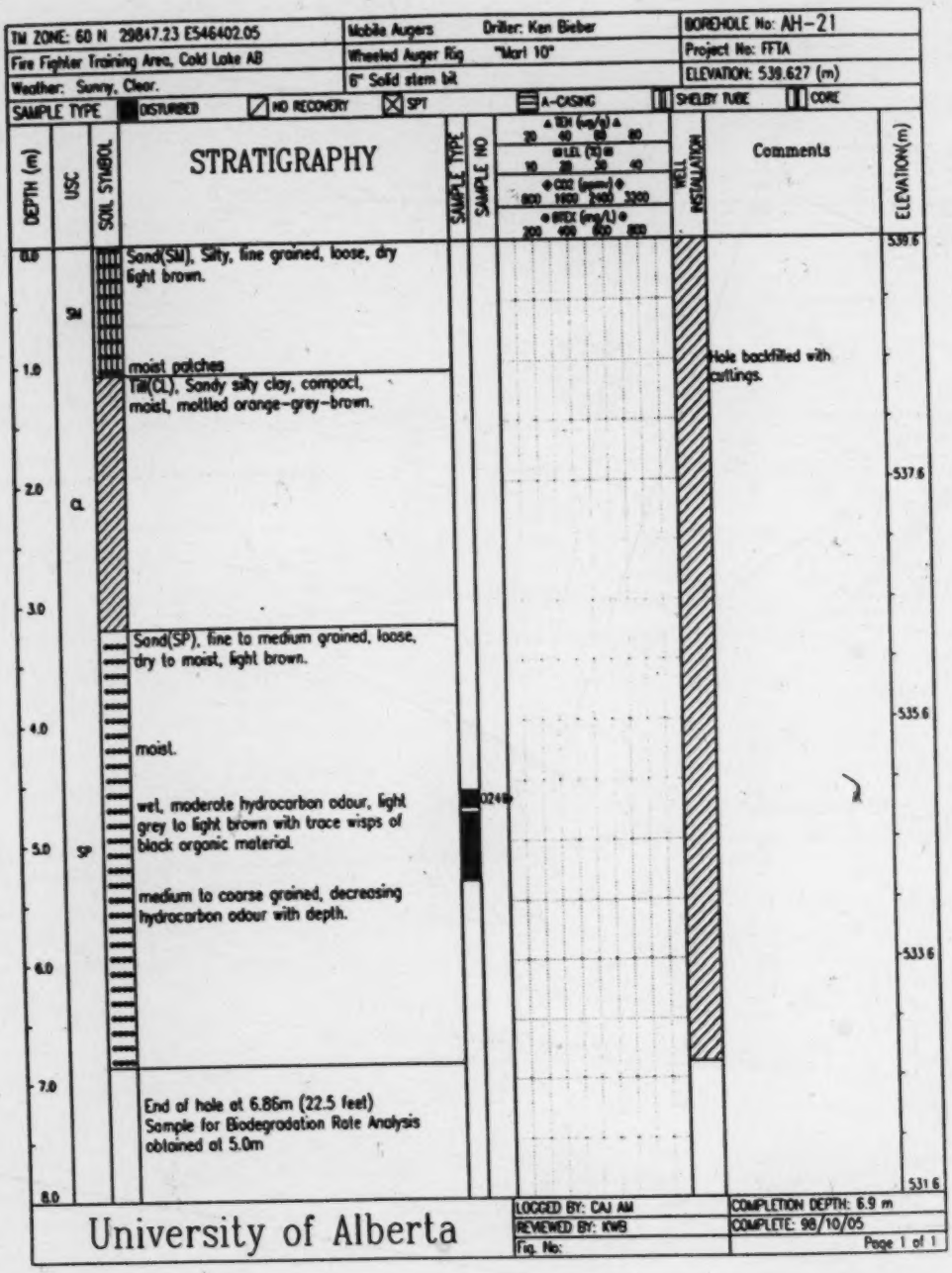
APPENDIX A

BOREHOLE LOGS


TM ZONE: 60 N 29847.23 E546402.05
Mobile Augers
Driller: Ken Bieber
BOREHOLE No: AH-21
Fire Fighter Training Area, Cold Lake AB
Wheeled Auger Rig "Mori 10"
Project No: FFTA
Weather: Sunny, Clear.
6" Solid stem bit
ELEVATION: 539.627 (m)
SAMPLE TYPE
DISTURBED
NO RECOVERY
SPT
A-CASING
SHELBY TUBE
CORE
DEPTH (m)
USC
SOIL SYMBOL
STRATIGRAPHY
SAMPLE TYPE
SAMPLE NO
WELL INSTALLATION
Comments
ELEVATION(m)
Sand(SM), Silty, fine grained, loose, dry light brown.
moist patches
Till(CL), Sandy silty clay, compact, moist, mottled orange-grey-brown.
Sand(SP), fine to medium grained, loose, dry to moist, light brown.
moist.
wet, moderate hydrocarbon odour, light grey to light brown with trace wisps of black organic material.
medium to coarse grained, decreasing hydrocarbon odour with depth.
End of hole at 6.86m (22.5 feet)
Sample for Biodegradation Rate Analysis obtained at 5.0m
Hole backfilled with cuttings.
539.6
537.6
535.6
533.6
531.6
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
SM
CL
SP
LOGGED BY: CAJ AM
REVIEWED BY: KWB
Fig. No:
COMPLETION DEPTH: 6.9 m
COMPLETE: 98/10/05
Page 1 of 1
University of Alberta

TM ZONE: 60 N 29866.90 E546408.77	Mobile Augers Driller: Ken Bieber	BOREHOLE No: MW-01
Fire Fighter Training Area, Cold Lake AB	Wheeled Auger Rig "Marl 10"	Project No: FFTA
Weather: Sunny, Hot.	5"ID Hollow stem bit, 3-3/8" Split Spoon	ELEVATION: 539.550 (m)

SAMPLE TYPE: DISTURBED | NO RECOVERY | SPT | A-CASING | SHELBY TUBE | CORE

DEPTH (m)	USC	SOIL SYMBOL	STRATIGRAPHY	SAMPLE TYPE	SAMPLE NO	SLOTTED PIEZOMETER	Comments	ELEVATION(m)
0.0	SM		Sand(SM), silty, fine to medium grained, trace gravel, loose, homogeneous,rootlets, dry becoming moist with depth, dark brown.					539.5
1.0								
2.0	CL		Till(CL), silty clay with some sand, trace gravel up to 1.5cm, subangular to subrounded, dense, weakly oxidized, weak hydrocarbon odour, green-grey (gleyed?). 1-1.5cm thick sand seam, coarse to medium grained, weakly oxidized, moist, no odour, brown. as above, some iron-stained fracture faces				Grout	537.5
3.0			push stone to 3.66m, no recovery.				Bentonite Pellets	
	CL		as above, no odour.					
4.0	SW		Sand(SW), fine to medium, trace silt and gravel, loose, moist to dry, homogeneous, light brown.					535.5
			No recovery from 4.57-5.33m.				Sand from formation	
5.0			sample tube wet from 4.88m.					
			Employ split spoon sampler below 5.33m. 5.33m: 30cm of light brown weakly oxidized fine-medium grained sand, weak hydrocarbon odour. 5.63m: 15cm of medium-coarse grained sand, homogeneous, light grey.		D07			
6.0	SW						Note: Solid Riser installed to 7.47m.	533.5
7.0			weak to moderate hydrocarbon odour.					
8.0			End of hole at 7.47m (24.5 feet) Sample for Microbial Enumeration obtained at 5.6m					531.5

University of Alberta

LOGGED BY: CAJ AM | REVIEWED BY: KWB | Fig. No:

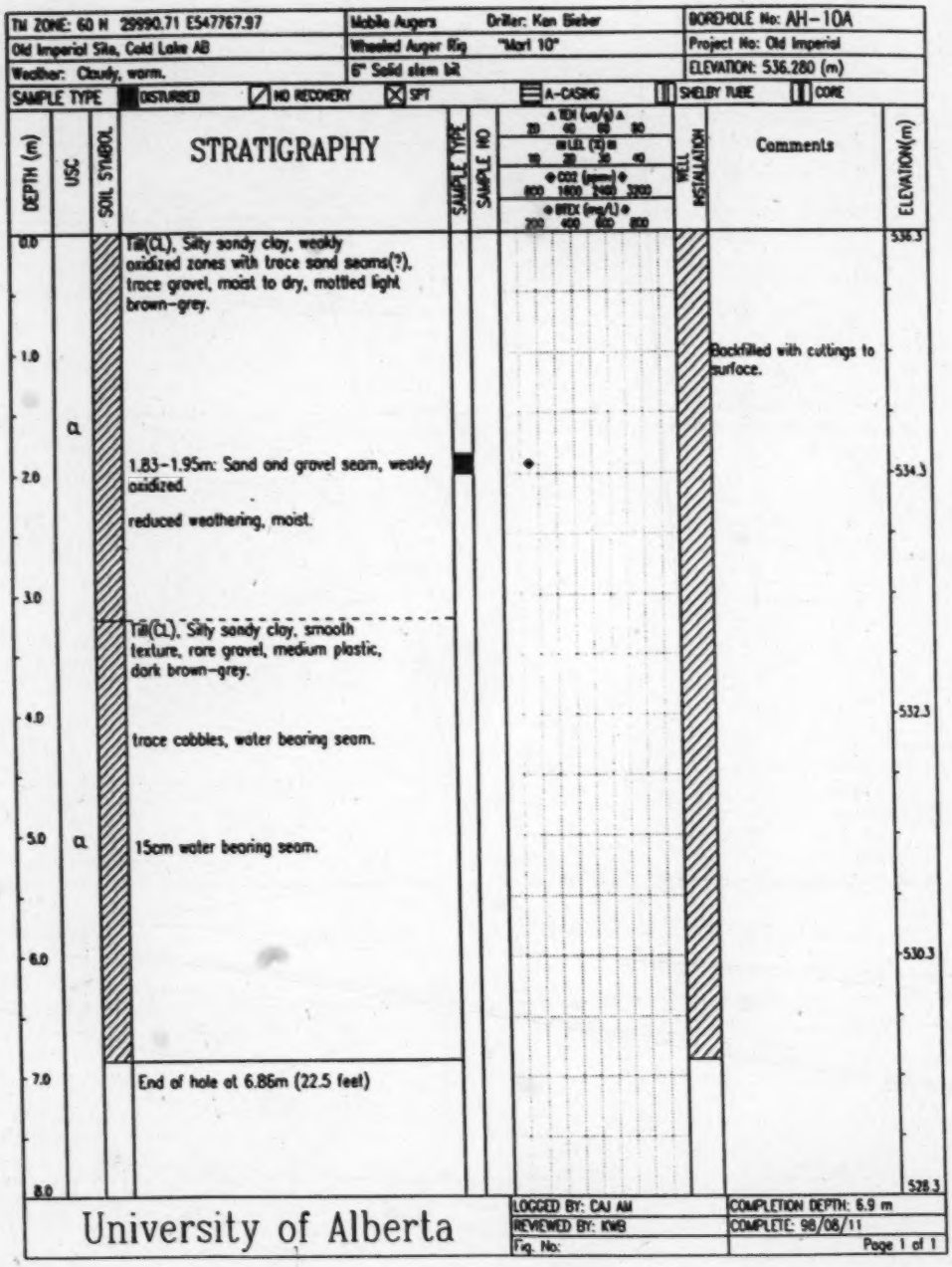
COMPLETION DEPTH: 7.5 m | COMPLETE: 98/06/12 | Page 1 of 1

TM ZONE: 60 N 29988.95 E547767.30	Mobile Augers Driller: Ken Bieber	BOREHOLE No: AH-10
Old Imperial Site, Cold Lake AB	Wheeled Auger Rig "Marl 10"	Project No: Old Imperial
Weather: Cloudy, warm.	5"ID Hollow stem bit, 3-3/8" Split Spoon	ELEVATION: 536.394 (m)

SAMPLE TYPE: DISTURBED | NO RECOVERY | SPT | A-CASING | SHELBY TUBE | CORE

DEPTH (m)	USC	SOIL SYMBOL	STRATIGRAPHY	SAMPLE TYPE	SAMPLE NO	WELL INSTALLATION	Comments	ELEVATION(m)
0.0	ML		Topsoil(ML), Sandy silt, trace pebbles, low plasticity, well developed soil profile, 1 thick, light grey.					536.4
1.0	CL		Till(CL), Silty sandy clay, moderate plasticity, no odour, dry, oxidized to 0.5m then grey, dry. rare angular gravel, smooth joint dipping 50 deg.				Backfilled with cuttings to surface.	
			push boulder, no recovery to 1.84m.					
2.0			Till (CL) as above. 5cm Sand & Gravel seam, sub-angular clasts to 2cm, no odour. compact to strong.					534.4
3.0	CL				D063			
			push boulder, no recovery to 3.81m.					
4.0	CL		Till (CL) as above, angular clasts to 1cm.					532.4
	CL		Till (CL-CI) Silty clay till, dark grey, homogeneous, smooth texture.					
5.0			End of hole at 4.57m (15 feet) Sample for microbial enumeration obtained at 3.00m.					530.4
6.0								
7.0								
8.0								528.4

University of Alberta	LOGGED BY: CAJ AM	COMPLETION DEPTH: 4.6 m
	REVIEWED BY: KWB	COMPLETE: 98/08/11
	Fig. No:	Page 1 of 1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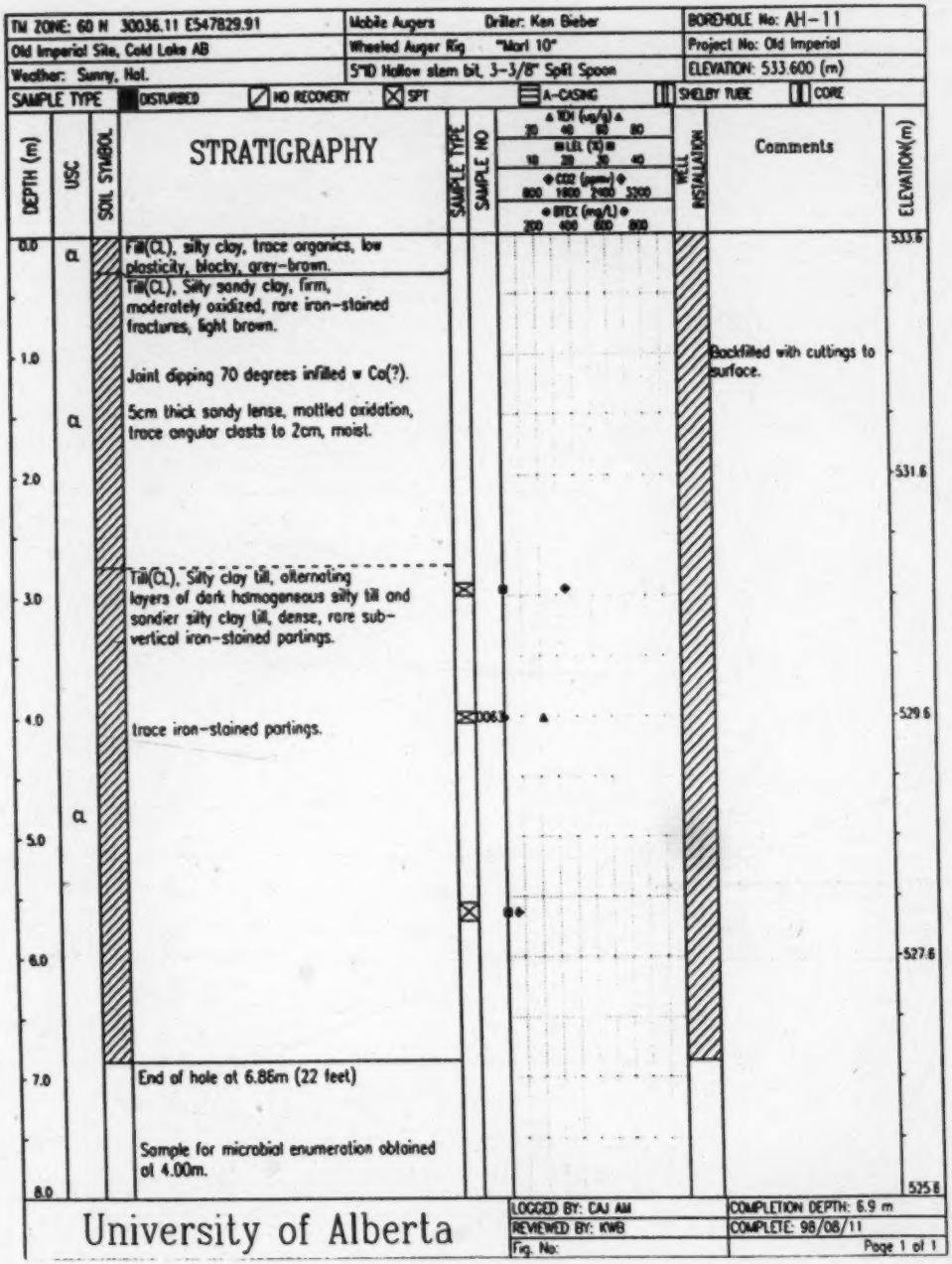
Mobile Augers
Driller: Ken Bieber
BOREHOLE No: AH-10A
Old Imperial Site, Cold Lake AB
Wheeled Auger Rig "Marl 10"
Project No: Old Imperial
Weather: Cloudy, warm.
6" Solid stem bit
ELEVATION: 536.280 (m)
SAMPLE TYPE
DISTURBED
NO RECOVERY
SPT
A-CASING
SHELBY TUBE
CORE
DEPTH (m)
USC
SOIL SYMBOL
STRATIGRAPHY
SAMPLE TYPE
SAMPLE NO
WELL INSTALLATION
Comments
ELEVATION(m)
Till(CL), Silty sandy clay, weakly oxidized zones with trace sand seams(?), trace gravel, moist to dry, mottled light brown-grey.
Backfilled with cuttings to surface.
1.83-1.95m: Sand and gravel seam, weakly oxidized.
reduced weathering, moist.
Till(CL), Silty sandy clay, smooth texture, rare gravel, medium plastic, dark brown-grey.
trace cobbles, water bearing seam.
15cm water bearing seam.
End of hole at 6.86m (22.5 feet)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
536.3
534.3
532.3
530.3
528.3
Gl
University of Alberta
LOGGED BY: CAJ AM
REVIEWED BY: KWB
Fig. No:
COMPLETION DEPTH: 6.9 m
COMPLETE: 98/08/11
Page 1 of 1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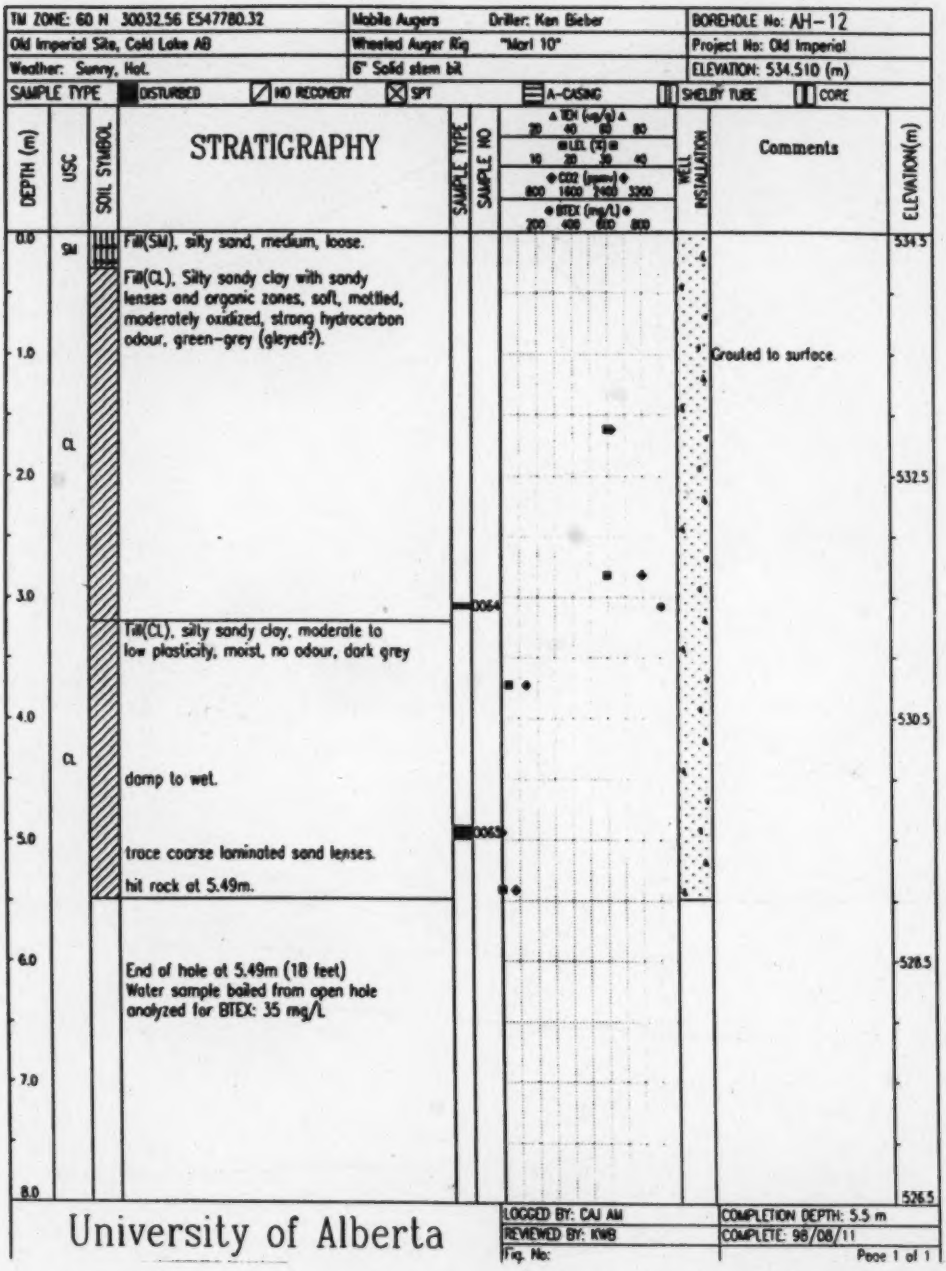
Mobile Augers
Driller: Ken Bieber
BOREHOLE No: AH-11
Old Imperial Site, Cold Lake AB
Wheeled Auger Rig "Mari 10"
Project No: Old Imperial
Weather: Sunny, Hot.
5"ID Hollow stem bit, 3-3/8" Split Spoon
ELEVATION: 533.600 (m)
SAMPLE TYPE
DISTURBED
NO RECOVERY
SPT
A-CASING
SHELBY TUBE
CORE
DEPTH (m)
USC
SOIL SYMBOL
STRATIGRAPHY
SAMPLE TYPE
SAMPLE NO
WELL INSTALLATION
Comments
ELEVATION(m)
Fill(CL), silty clay, trace organics, low plasticity, blocky, grey-brown.
Till(CL), Silty sandy clay, firm, moderately oxidized, rare iron-stained fractures, light brown.
Joint dipping 70 degrees infilled w Co(?).
5cm thick sandy lense, mottled oxidation, trace angular clasts to 2cm, moist.
Till(CL), Silty clay till, alternating layers of dark homogeneous silty till and sandier silty clay till, dense, rare sub-vertical iron-stained partings.
trace iron-stained partings.
End of hole at 6.86m (22 feet)
Sample for microbial enumeration obtained at 4.00m.
Backfilled with cuttings to surface.
533.6
531.6
529.6
527.6
525.6
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
University of Alberta
LOGGED BY: CAJ AM
REVIEWED BY: KWB
Fig. No:
COMPLETION DEPTH: 6.9 m
COMPLETE: 98/08/11
Page 1 of 1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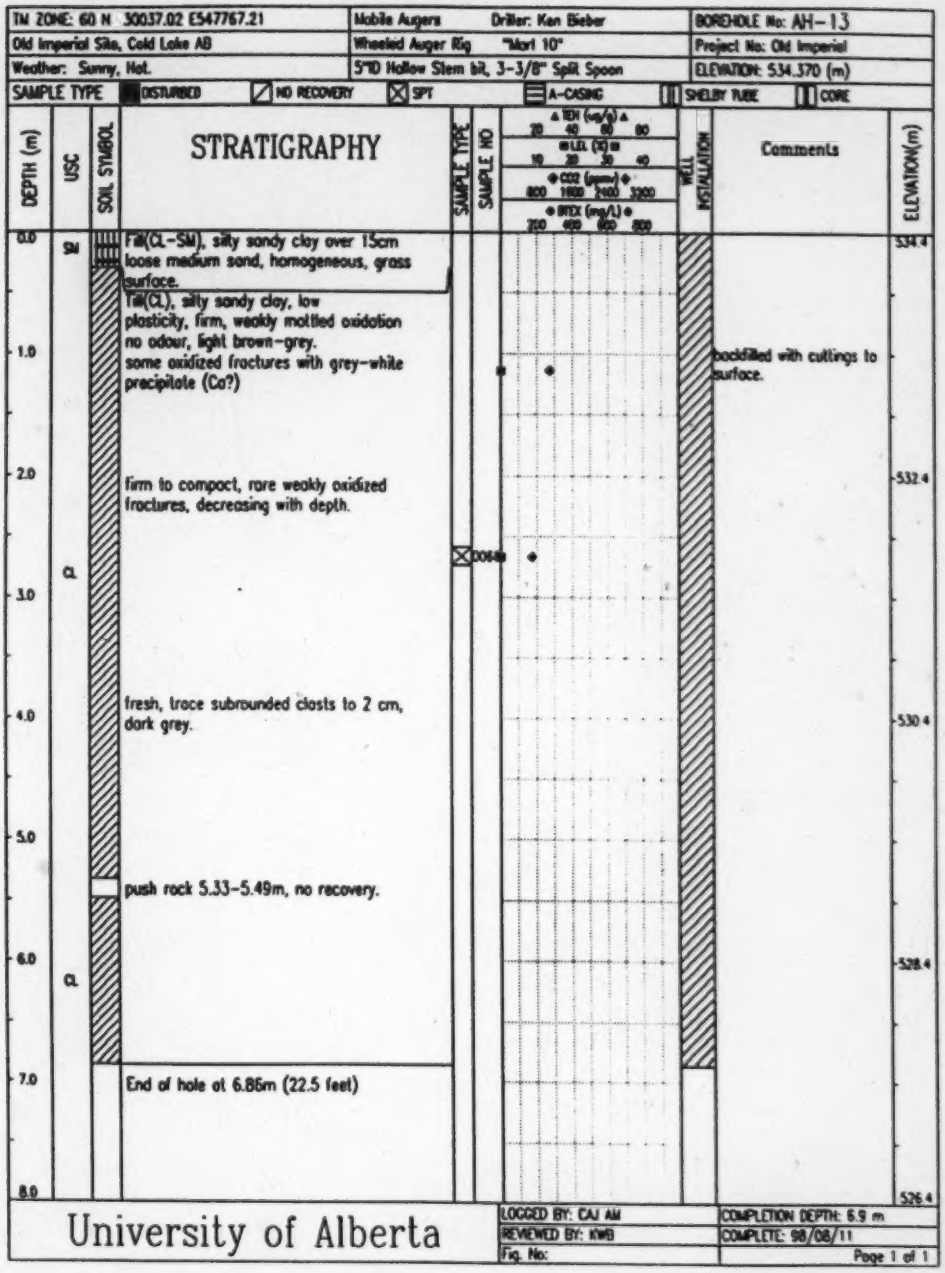
Mobile Augers
Driller: Ken Bieber
BOREHOLE No: AH-12
Old Imperial Site, Cold Lake AB
Wheeled Auger Rig "Mori 10"
Project No: Old Imperial
Weather: Sunny, Hot.
6" Solid stem bit
ELEVATION: 534.510 (m)
SAMPLE TYPE
DISTURBED
NO RECOVERY
SPT
A-CASING
SHELBY TUBE
CORE
DEPTH (m)
USC
SOIL SYMBOL
STRATIGRAPHY
SAMPLE TYPE
SAMPLE NO
WELL INSTALLATION
Comments
ELEVATION(m)
Fill(SM), silty sand, medium, loose.
Fill(CL), Silty sandy clay with sandy lenses and organic zones, soft, mottled, moderately oxidized, strong hydrocarbon odour, green-grey (gleyed?).
Grouted to surface
Fill(CL), silty sandy clay, moderate to low plasticity, moist, no odour, dark grey
damp to wet.
trace coarse laminated sand lenses.
hit rock at 5.49m.
End of hole at 5.49m (18 feet)
Water sample bailed from open hole analyzed for BTEX: 35 mg/L
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
SM
CL
534.5
532.5
530.5
528.5
526.5
University of Alberta
LOGGED BY: CAJ AM
REVIEWED BY: KWB
Fig. No:
COMPLETION DEPTH: 5.5 m
COMPLETE: 98/08/11
Page 1 of 1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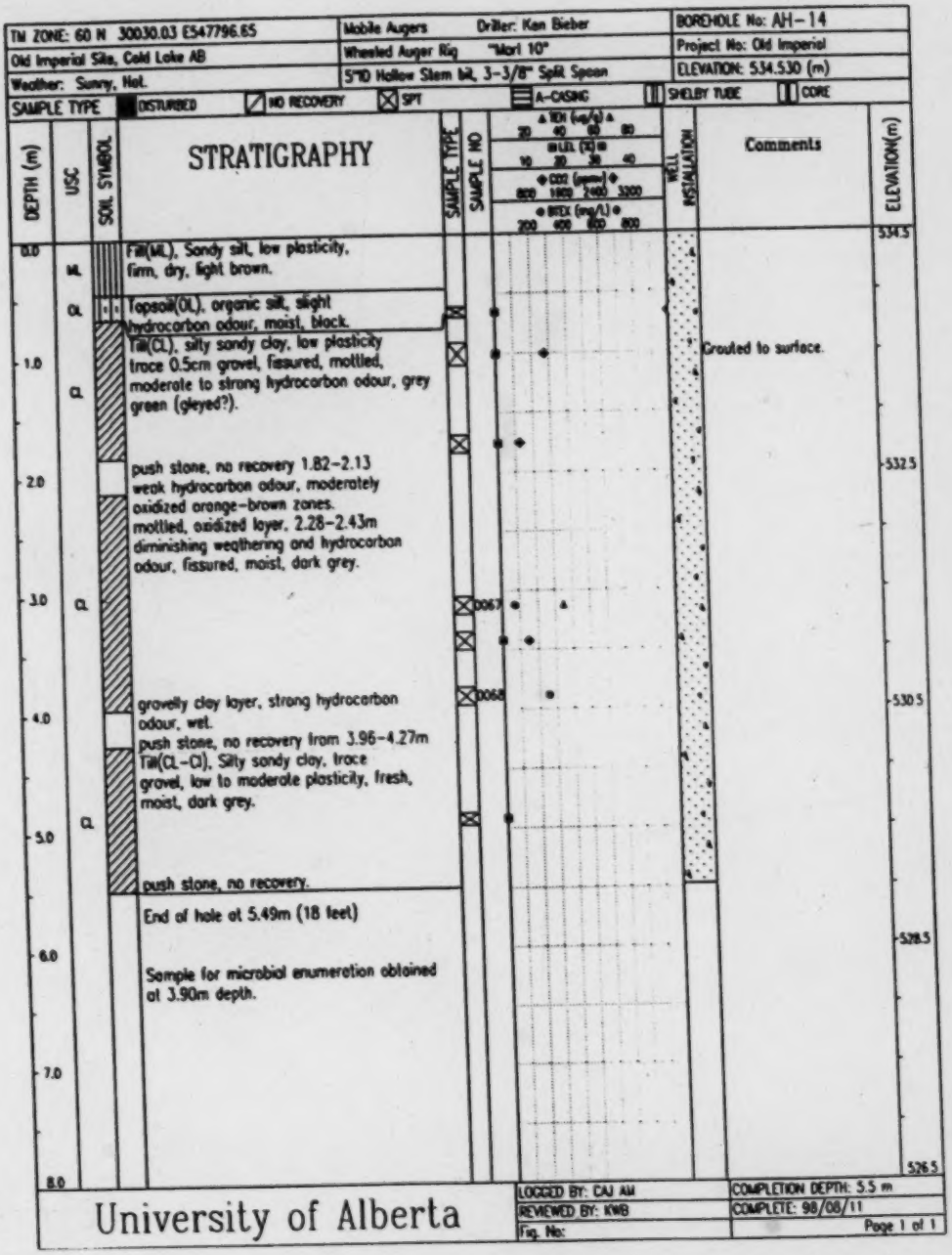
Mobile Augers
Driller: Ken Bieber
BOREHOLE No: AH-13
Old Imperial Site, Cold Lake AB
Wheeled Auger Rig "Mark 10"
Project No: Old Imperial
Weather: Sunny, Hot.
5"ID Hollow Stem bit, 3-3/8" Split Spoon
ELEVATION: 534.370 (m)
SAMPLE TYPE
DISTURBED
NO RECOVERY
SPT
A-CASING
SHELBY TUBE
CORE
DEPTH (m)
USC
SOIL SYMBOL
STRATIGRAPHY
SAMPLE TYPE
SAMPLE NO
TDH (kPa)
LEL (%)
CO2 (ppmv)
BTEX (mg/L)
WELL INSTALLATION
Comments
ELEVATION(m)
Fill(CL-SM), silty sandy clay over 15cm loose medium sand, homogeneous, grass surface.
Till(CL), silty sandy clay, low plasticity, firm, weakly mottled oxidation no odour, light brown-grey.
some oxidized fractures with grey-white precipitate (Ca?)
firm to compact, rare weakly oxidized fractures, decreasing with depth.
fresh, trace subrounded clasts to 2 cm, dark grey.
push rock 5.33-5.49m, no recovery.
End of hole at 6.86m (22.5 feet)
backfilled with cuttings to surface.
534.4
532.4
530.4
528.4
526.4
University of Alberta
LOGGED BY: CAJ AM
REVIEWED BY: KWB
Fig. No:
COMPLETION DEPTH: 6.9 m
COMPLETE: 98/08/11
Page 1 of 1


TM ZONE: 60 N 300303 E547796.65
Old Imperial Site, Cold Lake AB
Weather: Sunny, Hot.
Mobile Augers
Wheeled Auger Rig
5"ID Hollow Stem bit, 3-3/8" Split Spoon
Driller: Ken Bieber
"Mark 10"
BOREHOLE No: AH-14
Project No: Old Imperial
ELEVATION: 534.530 (m)
SAMPLE TYPE
DISTURBED
NO RECOVERY
SPT
A-CASING
SHELBY TUBE
CORE
DEPTH (m)
USC
SOIL SYMBOL
STRATIGRAPHY
SAMPLE TYPE
SAMPLE NO
WELL INSTALLATION
Comments
ELEVATION(m)
Fill(ML), Sandy silt, low plasticity, firm, dry, light brown.
Topsoil(OL), organic silt, slight hydrocarbon odour, moist, black.
Till(CL), silty sandy clay, low plasticity trace 0.5cm gravel, fissured, mottled, moderate to strong hydrocarbon odour, grey green (gleyed?).
Grouted to surface.
push stone, no recovery 1.82-2.13
weak hydrocarbon odour, moderately oxidized orange-brown zones.
mottled, oxidized layer, 2.28-2.43m
diminishing weathering and hydrocarbon odour, fissured, moist, dark grey.
D067
D068
gravelly clay layer, strong hydrocarbon odour, wet.
push stone, no recovery from 3.96-4.27m
Till(CL-Cl), Silty sandy clay, trace gravel, low to moderate plasticity, fresh, moist, dark grey.
push stone, no recovery.
End of hole at 5.49m (18 feet)
Sample for microbial enumeration obtained at 3.90m depth.
534.5
532.5
530.5
528.5
526.5
University of Alberta
LOGGED BY: CAJ AM
REVIEWED BY: KWB
Fig. No:
COMPLETION DEPTH: 5.5 m
COMPLETE: 98/08/11
Page 1 of 1

TM ZONE: 60 N 30028.53 E547795.89	Mobile Augers Driller: Ken Bieber	BOREHOLE No: MW-14A
Old Imperial Site, Cold Lake AB	Wheeled Auger Rig "Mori 10"	Project No: Old Imperial
Weather: Overcast, light rain.	5"ID Hollow stem bit, 3-3/8" Split Spoon	ELEVATION: 534.580 (m)

SAMPLE TYPE: DISTURBED | NO RECOVERY | SPT | A-CASING | SHELBY TUBE | CORE

DEPTH (m)	USC	SOIL SYMBOL	STRATIGRAPHY	SAMPLE TYPE	SAMPLE NO	SLOTTED PIEZOMETER	Comments	ELEVATION(m)
0.0								534.6
1.0			Drill with plug, no recovery to 3.05m					
2.0							Grout	532.6
3.0	CL		Till(CL), silty clay, trace gravel, weakly mottled oxidation, light/dark grey.				Bentonite Pellets	
			2mm sand seam, medium grained, moderate hydrocarbon odour.					
4.0	CL		push stone, no recovery 3.70–3.96m LEL = 31% downhole mottled weak oxidation, slight hydrocarbon odour, wet, dark grey.				Sand	530.6
			push stone, no recovery 4.57–4.72m					
5.0	CL		fresh till, some gravel, no odour.				Bentonite Chips	
			very dense, trace <1.5cm gravel and sand lenses, dark green-grey.				Solid Riser to end of hole (5.94m).	
6.0			End of hole at 5.94m (19.5 feet)					528.6
7.0								
8.0								526.6

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LOGGED BY: CAJ AM	COMPLETION DEPTH: 5.9 m
REVIEWED BY: KWB	COMPLETE: 98/08/12
Fig. No:	Page 1 of 1

TM ZONE: 60 N – E –	Mobile Augers Driller: Ken Bieber	BOREHOLE No: AH–15
Old Imperial Site, Cold Lake AB	Wheeled Auger Rig "Marl 10"	Project No: Old Imperial
Weather: Overcast, warm.	5"ID Hollow stem bit, 3–3/8" Split Spoon	ELEVATION: 0.000 (m)

SAMPLE TYPE ■ DISTURBED ⊘ NO RECOVERY ⊠ SPT ☰ A-CASING ▯▯ SHELBY TUBE ▯▯ CORE

DEPTH (m)	USC	SOIL SYMBOL	STRATIGRAPHY	SAMPLE TYPE	SAMPLE NO	▲ TEH (mg/g) ▲ 20 40 60 80 ● LEL (%) ● 10 20 30 40 ◆ CO2 (ppmv) ◆ 800 1600 2400 3200 ● BTEX (mg/L) ● 200 400 600 800	WELL INSTALLATION	Comments	DEPTH (m)
0.0									0.0
1.0			Drill with plug, no recovery to 1.52m.					Backfilled with grout.	
	CL		Till(CL), silty sandy clay, moderately oxidized, soft, grey to dark brown. push stone, no recovery 1.83–1.98m	⊠					
2.0			20cm of 0.5cm thick sand partings spaced 2–10cm, medium grained, trace gravel, moderate hydrocarbon odour.	⊠	007	▲			2.0
3.0			2.29m: 15cm silty sand layer, some gravel, moderate to strong hydrocarbon odour. reduced weathering, slight hydrocarbon odour. fresh, dense, dark grey.			● ◆			
4.0	CL								4.0
5.0									
6.0			End of hole at 5.33m (17.5 feet)						6.0
7.0									
8.0									8.0

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LOGGED BY: CAJ AM	COMPLETION DEPTH: 5.3 m
REVIEWED BY: KWB	COMPLETE: 98/08/12
Fig. No:	Page 1 of 1

TM ZONE: 60 N – E –	Mobile Augers Driller: Ken Bieber	BOREHOLE No: AH-22
Old Imperial Site, Cold Lake AB	Wheeled Auger Rig "Marl 10"	Project No: Old Imperial
Weather: Clear, warm.	6" Solid stem bit	ELEVATION: 0.000 (m)

SAMPLE TYPE: DISTURBED | NO RECOVERY | SPT | A-CASING | SHELBY TUBE | CORE

DEPTH (m)	USC	SOIL SYMBOL	STRATIGRAPHY	SAMPLE TYPE	SAMPLE NO	TDH (up/g) 20 40 60 80 / LEL (%) 10 20 30 40 / CO2 (ppmv) 800 1600 2400 3200 / BTEX (mg/L) 200 400 600 800	WELL INSTALLATION	Comments	DEPTH (m)
0.0	CL		Fill(CL), silty clay, loose, light brown.						0.0
1.0			Till(CL), silty sandy clay, trace gravel, dense, mottled, no odour, dry to moist, orange brown.					Backfill with cuttings to surface.	
2.0			reduced weathering, moist, dark brown.						2.0
3.0	CL		fresh till, dark green grey (gleyed?).						
4.0									4.0
5.0									
6.0			End of hole at 5.33m (17.5 feet)						6.0
7.0									
8.0									8.0

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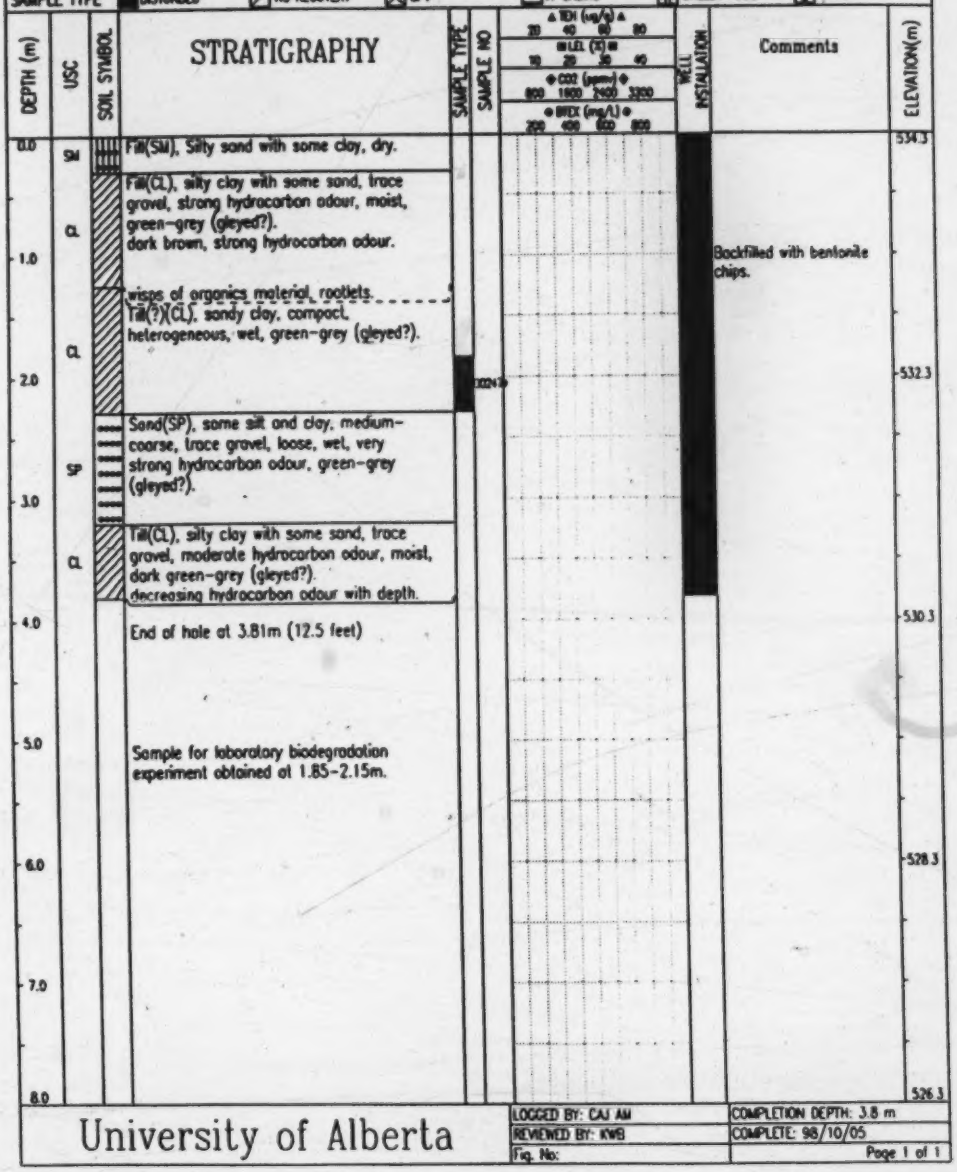
LOGGED BY: CAJ AM	COMPLETION DEPTH: 5.3 m
REVIEWED BY: KWB	COMPLETE: 98/10/05
Fig. No:	Page 1 of 1

TM ZONE: 60 N 30034.22 E547796.43	Mobile Augers Driller: Ken Bieber	BOREHOLE No: AH-23
Old Imperial Site, Cold Lake AB	Wheeled Auger Rig "Mori 10"	Project No: Old Imperial
Weather: Clear, warm.	6" Solid stem bit	ELEVATION: 534.320 (m)

SAMPLE TYPE: DISTURBED | NO RECOVERY | SPT | A-CASING | SHELBY TUBE | CORE



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LOGGED BY: CAJ AM | COMPLETION DEPTH: 3.8 m

REVIEWED BY: KWB | COMPLETE: 98/10/05

Fig. No: | Page 1 of 1

APPENDIX B

GEOLOGICAL ANALYSIS

DATA FOR WATER CONTENT AND FRACTION ORGANIC CARBON

TOC - Dry Weight Calculations

	Sample	Description	Boat mg	Sep-11 Boat +Wet mg	Sep-12 Dry weight mg - Day 1	Sep-14 Dry weight mg - Day 3	Wet Weight mg	Weight H2O mg (Day 3 data)	Moisture Content Weight $_{H2O}$/Weight $_{Soil}$	Avg
FFTA	FFTA 1 A	med-coarse	1.0	55.2	46.2	46.2	54.2	8.0	0.15	
	FFTA 1 B	sand	0.9	49.7	41.1	41.3	48.8	7.5	0.15	0.14
	FFTA 1 C		4.1	109.0	91.4	91.4	104.9	13.5	0.13	
FFTA	FFTA 2 A	med-coarse	1.0	24.9	20.2	20.3	23.9	3.6	0.15	
	FFTA 2 B	sand	0.9	30.1	24.3	24.4	29.2	4.8	0.16	0.16
Landfill	AH-07@6.5' A	silty sand	1.0	54.6	46.3	46.4	53.6	7.2	0.13	
	AH-07@6.5' B		1.1	52.1	43.9	44.0	51.0	7.0	0.14	0.13
	AH-07@6.5' C		4.1	125.3	106.2	106.2	121.2	15.0	0.12	
Landfill	AH-07@9' A	silty sand	1.0	60.8	49.6	49.7	59.8	10.1	0.17	
	AH-07@9' B		1.0	53.4	45.2	45.1	52.4	7.3	0.14	0.15
Old Imperial	AH-12@5' A	silty clay	1.0	46.0	35.7	35.7	45.0	9.3	0.21	
	AH-12@5' B		1.0	38.9	30.6	30.4	37.9	7.5	0.20	0.20
	AH-12@5' C		4.2	111.1	84.8	84.6	106.9	22.3	0.21	
Old Imperial	AH-15@7' A	silty clay	1.0	44.8	38.0	38.0	43.8	5.8	0.13	
	AH-15@7' B		1.0	46.1	38.0	38.0	45.1	7.1	0.16	0.14
	AH-15@7' C		4.1	99.1	82.1	82.0	95.0	13.0	0.14	

Balance: Mettler PC 8800 Delta Range
Furnace: 95°C
Into vented oven at 1600 hrs Sep 11

Additional Dry Weight Calculations for Soil Used in MPN Analysis

	Sample	Description	Boat mg	Aug 18 2pm Boat +Wet mg	Aug 19 10am Boat +Dry mg - Day 1	Aug 21 11am Boat + Dry mg - Day 3	Dry weight soil only-D3	Wet Weight mg	Weight H2O mg (w Day 3)	Water Content $Weight_{H2O}$:$Weight_{Soil}$	Avg
FFTA plume	AH-01 (1)	coarse sand	1.008	22.216	18.521	18.512	17.504	21.208	3.704	0.175	
	AH-01 (2)	lt gy bn	0.996	23.303	19.427	19.413	18.417	22.307	3.890	0.174	0.170
	AH-01 (3)		0.990	21.374	18.084	18.075	17.085	20.384	3.299	0.162	
Old Imperial upstream	AH-10 (1)	silty clay	1.000	20.403	17.002	16.921	15.921	19.403	3.482	0.179	
	AH-10 (2)	lt gy	1.010	29.762	24.539	24.454	23.444	28.752	5.308	0.185	0.188
	AH-10 (3)		1.007	30.643	24.800	24.720	23.713	29.636	5.923	0.200	
Old Imperial plume	AH-14 (1)	silty clay	0.998	35.436	28.462	28.365	27.367	34.438	7.071	0.205	
	AH-14 (2)	lt gy	0.997	42.40	33.826	33.74	32.743	41.403	8.660	0.209	0.212
	AH-14 (3)		1.01	35.14	27.683	27.60	26.59	34.130	7.540	0.221	
Old Imperial downstream	AH-11 (1)	silty clay	0.999	28.35	23.438	23.358	22.359	27.351	4.992	0.183	
	AH-11 (2)	lt gy	1.01	27.18	21.528	21.446	20.436	26.170	5.734	0.219	0.213
	AH-11 (3)		1.02	26.36	20.445	20.357	19.337	25.340	6.003	0.237	

Balance: Mettler PC 440
Furnace: 105°C
Into furnace at 1400 hrs Aug 18

Soil Fraction Organic Carbon Calculations

	Sample	Description	Crucible g	Cruc.+Dry g	Cruc.+cooked g - 24 hrs	Cruc.+cooked g - 48 hrs	Ash g	Ash Content %	Organic Matter %	Avg OM %
	FFTA 1 A	med-coarse	37.70	81.60	81.54	81.53	43.83	99.84	0.16	
FFTA	FFTA 1 B	sand	35.80	74.90	74.85	74.84	39.04	99.85	0.15	0.15
pit bottom	FFTA 1 C		23.09	78.29	78.22	78.21	55.12	99.86	0.14	
	FFTA 2 A	med-coarse	38.13	57.13	57.04	57.03	18.90	99.47	0.53	
FFTA	FFTA 2 B	sand	36.50	59.94	59.82	59.83	23.33	99.53	0.47	0.50
pit bottom										
	AH-12@5' A	silty clay	36.50	71.57	70.83	-	34.33	97.89	2.11	
Old Imperial	AH-12@5' B		35.44	64.99	62.74	-	27.30	92.39	7.61	2.51
plume	AH-12@5' C		35.90	61.41	60.88	60.67	24.77	97.10	2.90	
	AH-15@7' A	silty clay	35.86	73.25	72.63	72.71	36.85	98.56	1.44	
Old Imperial	AH-15@7' B		38.13	75.38	74.63	74.73	36.60	98.26	1.74	1.88
downstream	AH-15@7' C		25.60	63.52	62.89	62.59	36.99	97.55	2.45	

potential spillage - not incl. in avg

Method: ASTM D2974-87
Balance: Mettler PM 8800 in Undergrad Soils Lab
Muffle Furnace: 440°C
All samples cooled in desiccator prior to weighing

APPENDIX C

ALBERTA ENVIRONMENT

DATA FOR SEVEN SHALLOW MONITORING WELLS IN CENTRAL AND NORTHERN ALBERTA

Groundwater Data from Selected Shallow Monitoring Wells in Central and Northern Alberta

Site Name	Date	Depth m	Water Level m	Temp °C	pH	EC[1] uS/cm	Eh[2]	DO mg/L	SO4 mg/L	NO2-NO3 mg/L	COD[3] mg/L	Fe^{2+} mg/L	DIC[4] mg/L
Ardmore	6/8/94	5.49	2.49	5.60	7.07	210	-3	1.000	1.50	0.003	17	0.965	26.8
Devon Bot Gdn	3/16/95	7.01	3.72						25.00	8.030	11	0.007	42.0
Devon Bot Gdn (dup)	3/16/95	7.01	3.72	6.30	8.41	380	-299	1.550	26.00	8.720	13	0.022	41.3
Franchaise Bay	6/2/94	6.10	2.13	5.20	7.08	540	-91	0.550	9.00	0.003	83	21.500	91.8
Fort Vermillion N	6/23/94	7.64	3.41	5.60	7.68	1,000	6	0.630	54.00	0.003	30	1.640	44.7
Metiskow S	3/22/95	7.01	4.16	5.20	7.63	310	-210	1.800	12.00	0.003	6	0.226	42.4
Iron River	6/8/94	7.01	5.65	6.60	7.68	350	-10	3.900	1.50	0.003	5	0.004	52.3
Average Values*				5.8	7.6	465	-101	1.6	18.4	2.4	24	3.5	48.8

Source: Alberta Environment, High Quality Monitoring Network (unpublished)

* only duplicate included in arithmetic average

[1] EC = Electrical Conductivity

[2] Eh = Redox Potential

[3] COD = Chemical Oxygen Demand

[4] DIC = Dissolved Inorganic Carbon

APPENDIX D

MSDS SHEET FOR AQUEOUS FILM FORMING FOAM (AFFF) USED FOR FIRE FIGHTER TRAINING

3M Canada Company
Post Office Box 5757
London, Ontario N6A 4T1
Medical Emergency Telephone: (519)451-2500, Ext. 2222

Material Safety Data Sheet

Document id	: 10-3814-0	Issue date	: 04/12/1999
Version	: 17.00	Supersedes date	: 04/09/1999

Prepared by: Environmental Health and Safety Services Department, 3M Canada Company.
Telephone: (519) 452-6102, Fax: (519) 452-6015.

1 Product Identification

Tradename:
FC-203 LIGHT WATER (TM) AFFF 3% FP

Product ID:

CF-1206-0209-3	CF-1206-0210-1	CG-7900-7586-7	ZF-0002-0030-1
ZF-0002-0031-9	ZF-0002-0093-9	ZF-0002-0121-8	98-0211-0185-6
98-0211-7297-2	98-0211-7298-0	98-0280-1047-2	98-0280-1048-0
ZF-0002-0229-9	ZF-0002-0402-2	ZF-0002-0410-5	ZF-0002-0434-5
ZF-0002-0720-7	CF-1206-0975-9	XF-0008-0069-8	XP-0008-0070-6
ZF-0002-1127-4			

Intended Use of Product:
Product is a fire-extinguishing agent.

Division:
3M SPECIALTY MATERIALS

2 Composition/Information on Ingredients

Ingredient Name	CAS Number	Percentage
WATER	7732-18-5	36.0 - 40.0
DIETHYLENE GLYCOL BUTYL ETHER	112-34-5	35.0
ETHYLENE GLYCOL	107-21-1	20.0
RESIDUAL ORGANIC FLUOROCHEMICALS	Mixture	< 0.5
ALKYL SULFATE SALTS (2)	Trade Secret	1 - 5
AMPHORETIC FLUOROALKYLAMIDE DERIVATIVES (2)	Trade Secret	1 - 5
PERFLUOROALKYL SULFONATE SALTS (5)	Trade Secret	1 - 5

1

Ingredient Name	CAS Number	Percentage
TOLYL TRIAZOLE	29385-43-1	0.05

NOTE:
ALKYL SULFATE SALTS(2) is a Trade Secret. Refer to section 15 for further information.
AMPHOTERIC FLUOROALKYLAMIDE DERIVATIVES(2) is a Trade Secret. Refer to section 15 for further information.
PERFLUOROALKYL SULFONATE SALTS (5) is a Trade Secret. Refer to section 15 for further information.
Each percentage is expressed as the ratio of the weight of the ingredient to the weight of the controlled product.

3 Hazards Identification

Critical Hazards
Single overexposure, above recommended guidelines, may cause:
Central Nervous System Depression: signs/symptoms can include headache, dizziness, drowsiness, incoordination, slowed reaction time, slurred speech, giddiness and unconsciousness.
See Sections 7 and 11 for further information.

4 First Aid Measures

Instructions for Eye Contact:
Immediately flush eyes with large amounts of water. Get immediate medical attention.
Instructions for Skin Contact:
Flush skin with large amounts of water. If irritation persists, get medical attention.
Instructions for Inhalation:
If signs/symptoms occur, remove person to fresh air. If signs/symptoms continue, call a physician.
Instructions for Ingestion:
If swallowed, call a physician immediately. Only induce vomiting at the instruction of a physician. Never give anything by mouth to an unconscious person.

5 Fire Fighting Measures

Flash point:	None (Setaflash CC)
Lower Explosive Limit (%):	Not applicable
Upper Explosive Limit (%):	Not applicable
Autoignition temperature:	Not applicable

1

Suitable Extinguishing Media:
Product is a fire-extinguishing agent.
Exposure Hazards during Fire:

9 Physical and Chemical Properties

Physical form,Color,Odour:	liquid; clear; amber; slight solvent odour;
Odour Threshold:	No data available.
pH:	Approximately 8.5
Boiling point/boiling range:	100.00 C (Initial)
Melting point/melting range:	Not applicable
Vapour pressure:	Approximately 14.3 mmHg at 20 C
Water Solubility:	Miscible.
Partition coefficient (K o/w):	No data available.
Specific gravity:	Approximately 1.05 Water=1
Vapour density:	Approximately 1.21 Air=1 at 20 C
Volatile organic compounds:	578 gms/liter at 20 C
Evaporation rate:	< 1 BuOAc=1
Viscosity:	Unknown

10 Stability and Reactivity

Conditions to Avoid:
None known.
Materials to Avoid:
None known.
Hazardous Decomposition:
Carbon monoxide and carbon dioxide; hydrogen fluoride; Thermal decomposition of usage concentrations does not present a hazard. Toxic vapours, gases or particulates;

1

Stability and Reactivity:
Stable. Hazardous polymerization will not occur.

11 Toxicological Information

Effects from Eye Contact:
Mild Eye Irritation: signs/symptoms can include redness, swelling, pain, and tearing.
Effects from Skin Contact:
Mild Skin Irritation (after prolonged or repeated contact): signs/symptoms can include redness, swelling, and itching.
Effects from Inhalation:
Single overexposure, above recommended guidelines, may cause:
Central Nervous System Depression: signs/symptoms can include headache, dizziness, drowsiness, incoordination, slowed reaction time, slurred speech, giddiness and unconsciousness. Irritation (upper respiratory): signs/symptoms can include soreness of the nose and throat, coughing and sneezing.

APPENDIX E

ENVIRO-TEST LABORATORIES

CHEMICAL ANALYSES METHODOLOGIES

Acid Digestion

Preparation: Microwave digestion of sample in a closed vessel with concentrated nitric acid on water samples.
Reference: E.P.A. SW 846 Method 3015

Balance

Instrumental Method: Sum(Anions)/Sum(Cations)*100
Method Reference: APHA 1030 F

Bicarbonate (HCO3)

Instrumental Method: Calculated from Alkalinity
Method Reference: APHA 2320B

BTEX in Water

PREPARATION METHOD: Purge and trap extraction.

INSTRUMENTAL METHOD: GC/PID

METHOD REFERENCE: Modified SW-846 USEPA Method 5030 and 8020.

QC SUMMARY:

Accuracy	Precision
100%	+/- 10%

NOTE: Accuracy is expressed as the average % recovery and Precision as the relative standard deviation (RSD) of fortifications made using certified standards (BTEX).

BTEX and TVH in Soil

PREPARATION METHOD: Methanol extraction with headspace analysis.

INSTRUMENTAL METHOD: GC/PID for BTEX.
GC/FID for TVH - summation of hydrocarbons from C5 to C10 carbon range and is calculated against a BTEX standard.
NOTE: Results based upon dry weight.

METHOD REFERENCE: Modified SW-846 USEPA Method 5021 and 8015/8020.

BTEX QC SUMMARY:

Accuracy	Precision
93%	+/- 23%

NOTE: Accuracy is expressed as the average % recovery and Precision as the relative standard deviation (RSD) of fortifications made using certified standards (BTEX).

TVH QC SUMMARY:

Accuracy	Precision
96%	+/- 24%

NOTE: Accuracy is expressed as the average % recovery and Precision as the relative standard deviation (RSD) of fortifications made using certified standards (BTEX).

Chloride (Cl)

Preparation: Filter through 0.45u filter
Instrumental: Sample analyzed colorimetrically @ 480 nm using ferricyanide method on a Cobas Fara discrete analyzer
Reference: APHA 4500-Cl, E

or

Preparation Method: 0.45µ filtration if turbid
Instrumental Method: Ion Chromatography
Method Reference: APHA 4110 B

Carbonate (CO3)

Instrumental Method: Calculated from Alkalinity
Method Reference: Carbonate APHA 2320B

Conductance (EC)

Instrumental Method: Conductivity Meter
Method Reference: Conductance APHA 2510B

Ferrous Iron, Extractable

Preparation: Preserve with HCl to pH <4, store in vial with no headspace.
Instrumental: The sample is analyzed by IC with a UV/VIS detector and PAR color reagent. Alternatively, for high values, the extract is analyzed also by ICP, and the ferrous iron is determined by difference (ICP Fe - Fe+3)
Method Reference: Dionex Technical Note #10

Ferric Iron, HCL Extract.

Preparation: 10 g of wet soil is sonicated for 1 hour with 50 ml 1N HCl extracting solution under a nitrogen blanket.
Instrumental: The extractant is analyzed by IC with a UV/VIS detector and PAR color reagent. Alternatively, for high values, the extract is analyzed also by ICP, and the ferric iron is determined by difference (ICP Fe - Fe+2)
Method Reference: Dionex Technical Note #10

Hardness

Instrumental Method: Calculated from Ca+Mg as CaCO3
Method Reference: Hardness APHA 2340 B

ICP Metals Setup

PREPARATION METHOD:

Dissolved: Filter through 0.45u and preserve with nitric acid
Extractable: Preserve with nitric acid
Total: Preserve with nitric acid; digest with nitric/hydrochloric acid

INSTRUMENTAL METHOD: ICP Spectrophotometry
METHOD REFERENCE: APHA 3120B/3030F, Standard Methods; 18th ed.

Routine Metals

PREPARATION METHOD: Filter through 0.45u and preserve with nitric acid
INSTRUMENTAL METHOD: ICP Spectrophotometry
METHOD REFERENCE: APHA 3120B/3030F, Standard Methods; 18th ed.

Sulfur reported as sulfate. ICP result multiplied by 3 to convert.

Sulfate (SO4)

Preparation Method: 0.45 u filtraton if turbid
Instrumental Method: Ion Chromatography or ICP
Method Reference: S04 Dionex Handbook of Ion Chromatography pg 37.

% Moisture

Preparation Method: Sample is oven dried at 105 degrees C
Instrumental Method: Gravimetric analysis

Nitrate+Nitrite (N)

Preparation Method: 0.45µ Filtration
Instrumental Method: Automated colorimetry (Cobas Fara Discrete analyzer)
Hydrazine reduction @ 520 nm
Method Reference: APHA 4500-NO3-H

or

Preparation Method: 0.45µ filtration if turbid
Instrumental Method: Ion Chromatography
Method Reference: APHA 4110 B
and
Preparation Method: 0.45µ filtration if turbid
Instrumental Method: Ion Chromatography
Method Reference: APHA 4110 B

Hydroxide

Method Reference: Hydroxide APHA 2320 B

pH in Water

Instrumental Method: pH Meter
Method Reference: APHA 4500-H+ B

Sulphide

Instrumental Method: Automated continuous flow with dialysis
and colorimetry at 600 nm
Method Reference: Sulphide

Total Alkalinity

Instrumental Method: If pH<8.3 on the initial sample, titration for alkalinity will be performed to pH 8.3 and 4.5 endpoint, using autotitrator or manual technique.

Method Reference: T ALK APHA 2320B

TDS (Calculated)

Instrumental Method: Calculated from the sum of ions
Method Reference: TDS APHA 1030 F

Total Extractables (Soil)

PREPARATION METHOD: Shake and sonication extraction with organic solvent

INSTRUMENTAL METHOD: GC/FID - summation of hydrocarbons from C11 to C30 carbon range (excluding benzene, toluene, ethylbenzene, and xylenes) and calculated against diesel standard.
NOTE: Results based upon dry weight.

METHOD REFERENCE: Modified SW-846 USEPA Method 3550/3580 and 8000

QC SUMMARY:

Accuracy	Precision
111%	+/- 24%

NOTE: Accuracy is expressed as the average % recovery and Precision as the relative standard deviation (RSD) of fortifications made using in-house standards (TEH).

Total Kjeldahl Nitrogen

Total Organic Carbon

Instrumental Method: Combustion - Infrared carbon analyzer

Phosphorus, Total

Preparation Method: Persulphate/ Sulfuric Acid tube digest
Instrumental Method: Automated colorimetry (Cobas Fara discrete analyzer) Asorbic acid reduction
Method Reference: Phosphorous, Total APHA 4500-P B,E
Cobas Fara II water testing Application

Vol. Organics (MS):Solids

Preparation Method: Autcmated headspace

Instrument Method: GC/MS analysis

Method Reference: Extraction Method: EPA 5021 (modified)
Analytical Method: EPA 8240 (modified)

Interferences: *** Values for 1,1,2,2-tetrachloroethane and trichloroethene may not accurately reflect concentrations present in the sample(s) due to the decomposition of the former to the latter when exposed to heat and pressure. (See MOEE Method PETHC-E3132A, 1.5.1.5 Dehydrohalogenation)

Volatile Organics (MS):H20

Preparation Method: Automated headspace

Instrument Method: GC/MS analysis

Method Reference: Extraction Method: EPA 5021 (modified)
Analytical Method: EPA 8240 (modified)

Interferences: *** Values for 1,1,2,2-tetrachloroethane and trichloroethene

may not accurately reflect concentrations present in the sample(s) due to the decomposition of the former to the latter when exposed to heat and pressure. (See MOEE Method PETHC-E3132A, 1.5.1.5 Dehydrohalogenation)

THIS IS THE LAST PAGE OF THE METHODOLOGY APPENDIX.

APPENDIX F

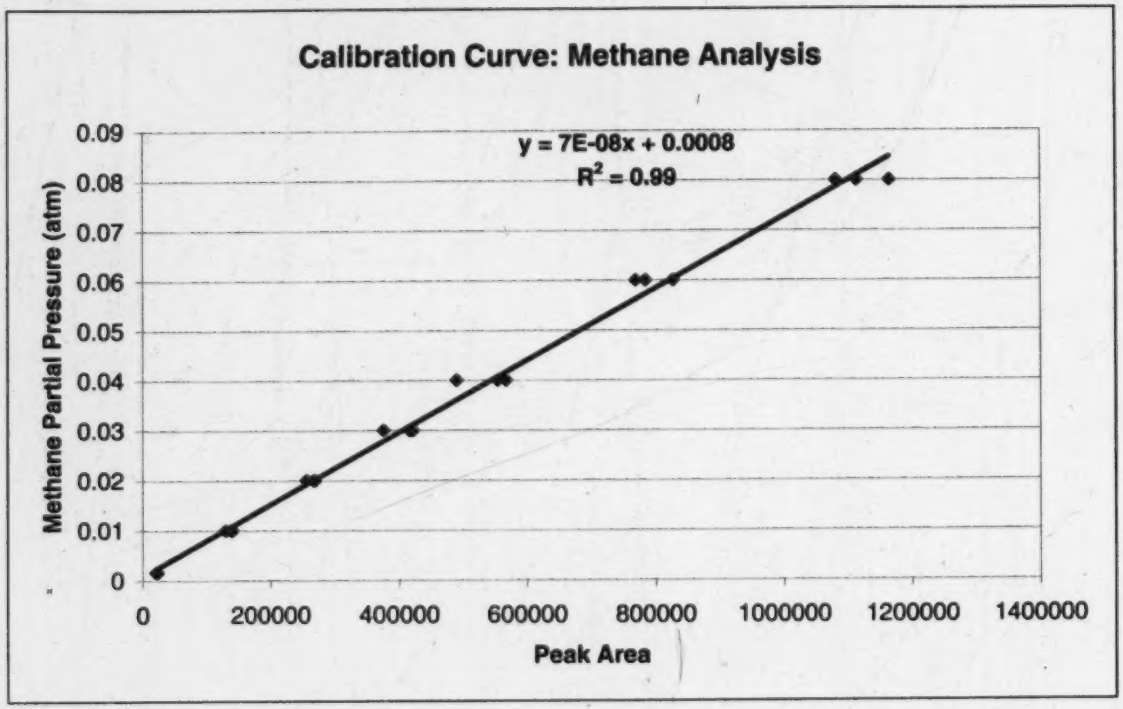
GROUNDWATER ANALYSIS

DISSOLVED METHANE CALIBRATION CURVE AND DATA FOR GAS CHROMATOGRAPHIC ANALYSIS

METHANE STANDARD CURVE DATA

Temperature (deg C): 25
Henry's Constant (atm*L/mol 13.411 x 10^{-4}
r CH_4 (g/L): 0.7174
MW (g/moL) 16.04
mole air: 0.0067
Assume STP 1 atm 0 deg C

% CH_4	VOLUME INJECTED (mL)	PEAK AREA	MOLE METHANE (mol)	MOLE FRACTION (x_g)	PARTIAL PRESSURE
0.16	0.00025	23300	1.12E-08	1.67E-06	0.0016
0.16	0.00025	20600	1.12E-08	1.67E-06	0.0016
0.16	0.00025	21976	1.12E-08	1.67E-06	0.0016
1	0.0016	129220	7.16E-08	1.07E-05	0.01
1	0.0016	138030	7.16E-08	1.07E-05	0.01
1	0.0016	139870	7.16E-08	1.07E-05	0.01
2	0.0032	256090	1.43E-07	2.13E-05	0.02
2	0.0032	266990	1.43E-07	2.13E-05	0.02
2	0.0032	269250	1.43E-07	2.13E-05	0.02
3	0.0049	375760	2.19E-07	3.27E-05	0.03
3	0.0049	421210	2.19E-07	3.27E-05	0.03
3	0.0049	416340	2.19E-07	3.27E-05	0.03
4	0.0066	554440	2.95E-07	4.40E-05	0.04
4	0.0066	489670	2.95E-07	4.40E-05	0.04
4	0.0066	567370	2.95E-07	4.40E-05	0.04
6	0.0101	784720	4.52E-07	6.73E-05	0.06
6	0.0101	827330	4.52E-07	6.73E-05	0.06
6	0.0101	769410	4.52E-07	6.73E-05	0.06
8	0.01374	1E+06	6.15E-07	9.16E-05	0.08
8	0.01374	1E+06	6.15E-07	9.16E-05	0.08
8	0.01374	1E+06	6.15E-07	9.16E-05	0.08


Calibration Curve: Methane Analysis
y = 7E-08x + 0.0008
R2 = 0.99
Methane Partial Pressure (atm)
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
200000
400000
600000
800000
1000000
1200000
1400000
Peak Area

Dissolved Methane Calculations

Temperature:	25 deg C
Molecular weight	16 g/mol
Headspace Volume (Vg)	4 ml
Liquid Volume (Vw)	39.8 ml
Henry's Constant	41300 dimensionless

$$C = MW\left[\frac{55.5}{H} + \frac{V_g}{V_w}\frac{1}{22.4}\frac{273}{(T+273)}\right]X_g$$

	WELL	REPLICATE	PEAK AREA	CONCENTRATION	Average Concentration (mg/L)	Average Concentration (mg/L) rounded
FFTA	HP-1	1	46053	0.00402	0.351	0.3
		2	42460	0.00377	0.329	
		3	45561	0.00399	0.348	
FFTA	HP-2	1	1034400	0.07321	6.390	6.3
		2	1009100	0.07144	6.234	
FFTA	HP-03	1	27257	0.00271	0.236	0.2
		2	27378	0.00272	0.237	
		3	26987	0.00269	0.235	
FFTA	MW-L (15 EBA)	1	1200200	0.08481	7.401	7.4
		2	1216000	0.08592	7.498	
		3	1195200	0.08446	7.371	
FFTA	MW-K (16 EBA)	1	123780	0.00948	0.826	0.8
		2	126600	0.00968	0.843	
		3	131550	0.01001	0.873	
OLD IMPERIAL	MW-167-3	1	31313	0.00299	0.261	0.3
		2	33122	0.00312	0.272	
		3	34419	0.00321	0.280	
OLD IMPERIAL	MW-97-2	1	0	0.00080	0.070	0.0
OLD IMPERIAL	AH-15	1	284110	0.01929	1.683	1.6
		2	256170	0.01873	1.635	
		3	248540	0.01820	1.588	
OLD IMPERIAL	MW-9109-1	1	0	0.00080	0.070	0.0
OLD IMPERIAL	MW-H	1	79007	0.00633	0.552	0.6
		2	87382	0.00692	0.604	
		3	91524	0.00721	0.629	
		4	83421	0.00664	0.579	
OLD IMPERIAL	MW-97-6	1	27658	0.00274	0.239	0.2
		2	19111	0.00214	0.187	
		3	14945	0.00185	0.161	
OLD IMPERIAL	MW-97-3	1	25593	0.00259	0.226	0.2
		2	18978	0.00213	0.186	
		3	12397	0.00167	0.146	
OLD IMPERIAL	MW-CF-6	1	0	0.00080	0.070	0.0
OLD IMPERIAL	MW-9109-9	1	0	0.00080	0.070	0.0
OLD IMPERIAL	MW-G (167-2)	1	43456	0.00384	0.335	1.1
		2	44486	0.00391	0.341	
		3	424444	0.03051	2.663	

Notes:
- Liquid Volume is avg from three measurements in graduated cylinder
- Zero (0) Peak area results in 0.07 mg/L methane due to offset of Standard Curve
- This value has been entered as 0 in Average Conc. column

APPENDIX G

MICROBIAL ENUMERATION

MOST PROBABLE NUMBER (MPN) CALCULATIONS AND LIQUID MEDIA RECIPES

Media Used for Each Group of Microorganisms

Group being Enumerated	Medium	Positive Culture Used
Total Heterotrophs	R2A liquid, full strength	A heterotrophic bacterial culture
JP-4 degraders	Bushnell-Haas, plus 50uL filter-sterilized JP-4	An 8°C JP-8 maintenance culture
Sulfate Reducers	Modified Butlin's broth, with nails	AL-1
Nitrate Reducers	Difco Nitrate broth, with inverted Durham vials	*Pseudomonas aeruginosa, Proteus vulgaris.*
Iron Reducers	B10 medium	*Shewanella putrefaciens*

Liquid Media Recipes

R2A Liquid (Total Heterotrophs)

Source: Adapted from Atlas, Ronald. 1993. Handbook of Microbiological Media, ed. Lawrence C Parks. Boca Raton, FL: CRC press.

per litre doubly glass distilled water

0.5g	Yeast Extract	0.3g	Sodium Pyruvate
0.5g	Casamino Acid	0.25g	Tryptone
0.5g	Glucose	0.25g	Peptone
0.5g	Soluble Starch	0.024g	$MgSO_4$, anhydrous
0.3g	K_2HPO_4		

Final pH 7.2

Bushnell-Haas (JP-4 degraders)

Source: Difco Manual, 1984. Dehydrated Culture Media and Reagents for Microbiology. 10th ed. Difco Laboratories, Detroit, MI.

per litre doubly glass distilled water

0.2g	$MgSO_4$	1g	Dipotassium Phosphate
0.02g	CaCl	1g	Ammonium Nitrate
1g	Monopotassium Phosphate	0.05g	Ferric Chloride

Final pH 7.0

Modified Butlin's (Sulfate reducers)

Source: modified from Butlin, et al., 1949. Journal of General Microbiology, 3:46-49.

per litre doubly glass distilled water

0.5g	K_2HPO_4	1g	NaCl
1g	NH_4Cl	0.5g	Sodium Benzoate
2g	Na_2SO_4	2.1g	Sodium Pyruvate
1g	$MgSO_4.7H_2O$	1g	Yeast Extract
0.07g	$CaCl_2.2H_2O$	0.004g	$FeSO_4.7H_2O$
2.5ml	60% Sodium Lactate	10ml	Resazurin
2g	Sodium Acetate		

Difco Nitrate Broth

Source: Difco Manual, 1984. Dehydrated Culture Media and Reagents for Microbiology. 10th ed. Difco Laboratories, Detroit, MI.

per litre doubly glass distilled water

3g	Bacto Beef Extract
5g	Bacto Peptone
1g	Potassium Nitrate

Final pH 7.0

B10 Medium

Source: C.O. Obuekwe, Ph.D. thesis, 1980, University of Alberta.

per litre doubly glass distilled water

0.8g	K_2HPO_4	10ml	$CaSO_4$ (saturated)
0.2g	KH_2PO_4	5g	Yeast Extract
0.2g	$MgSO_4.7H_2O$	5g	Bacto peptone
0.2g	NaCl	4.7g	$FePO_4$
1ml	0.1% $MnSO_4$	2.5g	Agar
1ml	0.1% $NaMO_4$		

50X Nutrient Stock

per litre doubly glass distilled water

25g	K_2HPO_4
50g	NH_4Cl
100g	KNO_3

Microbial Enumeration Data for FFTA and Old Imperial Site

Calculated at Week Six (following 4 weeks at 6degC and 2 weeks at 22degC

Site	Test	Char # *	Dilution	MPN			Dilution correction	Soil mass correction	wet/dry soil ratio	Soil Moisture Correction	95% Confidence Interval	
			first value	min (95%C.I.)	max (95%CI)	Expected	MPN/g wet soil added	MPN/g wet soil		MPN/g dry soil	MPN min #/g dry wt	MPN max #/g dry wt
FFTA AH-01	NRB >nitrite	5-5-4	1.00E-05	40.0	460.0	160	1.60E+07	1.59E+07	1.21	1.9E+07	4.8E+06	5.5E+07
	NRB >N_2 gas	5-5-4	1.00E-05	40.0	460.0	160	1.60E+07	1.59E+07	1.21	1.9E+07	4.8E+06	5.5E+07
	FeRB	5-2-0	1.00E-02	1.5	14.9	4.9	4.90E+02	486	1.21	5.9E+02	1.8E+02	1.8E+03
	SRB	0-0-0							1.21	0.0E+00		
	JP-4	5-4-1	1.00E-04	6.0	39.0	17	1.70E+05	1.69E+05	1.21	2.0E+05	7.2E+04	4.7E+05
	Total Het	5-5-3	1.00E-05	23.0	253.0	92	9.20E+06	9.16E+06	1.21	1.1E+07	2.8E+06	3.0E+07
O.I. Downstream AH-11	NRB >nitrite	5-5-5	1.00E-05	40.0	460.0	160	1.60E+07	1.59E+07	1.27	2.0E+07	5.0E+06	5.8E+07
	NRB >N_2 gas	5-3-0	1.00E-05	2.3	22.0	7.9	7.90E+05	7.84E+05	1.27	1.0E+06	2.9E+05	2.8E+06
	FeRB	4-0-0	1.00E-01	0.4	3.4	1.3	1.30E+01	1.29E+01	1.27	1.6E+01	5.0E+00	4.3E+01
	SRB	0-0-0				0	0.00E+00	0.00E+00	1.27	0.0E+00		
	JP-4	5-4-1	1.00E-03	6.0	39.0	17	1.70E+04	1.69E+04	1.27	2.1E+04	7.6E+03	4.9E+04
	Total Het	5-5-2	1.00E-05	15.0	166.0	54	5.40E+06	5.36E+06	1.27	6.8E+06	1.9E+06	2.1E+07
O.I. Plume AH-14	NRB >nitrite	5-3-1	1.00E-05	3.0	24.0	11	1.10E+06	1.09E+06	1.27	1.4E+06	3.8E+05	3.0E+06
	NRB >N_2 gas	5-4-0	1.00E-04	3.0	35.0	13	1.30E+05	1.29E+05	1.27	1.6E+05	3.8E+04	4.4E+05
	FeRB	5-0-0	1.00E-01	0.7	6.6	2.3	2.30E+01	2.29E+01	1.27	2.9E+01	8.8E+00	8.3E+01
	SRB	0-0-0	1.00E-01			0	0.00E+00	0.00E+00	1.27	0.0E+00		
	JP-4	5-2-0	1.00E-01	1.5	14.9	4.9	4.90E+01	4.87E+01	2.27	1.1E+02	3.4E+01	3.4E+02
	Total Het	5-0-0	1.00E-05	0.7	6.6	2.3	2.30E+05	2.29E+05	1.27	2.9E+05	8.8E+04	8.3E+05
O.I Background AH-10	NRB >nitrite	5-0-0	1.00E-05	0.7	6.6	2.3	2.30E+05	2.27E+05	1.23	2.8E+05	8.5E+04	8.0E+05
	NRB >N_2 gas	5-0-0	1.00E-05	0.7	6.6	2.3	2.30E+05	2.27E+05	1.23	2.8E+05	8.5E+04	8.0E+05
	FeRB	5-0-0	1.00E-01	0.7	6.6	2.3	2.30E+01	2.27E+01	1.23	2.8E+01	8.5E+00	8.0E+01
	SRB	0-0-0										
	JP-4	5-3-2	1.00E-03	5.0	35.0	14	1.40E+04	1.38E+04	1.23	1.7E+04	6.1E+03	4.2E+04
	Total Het	5-0-0	1.00E-05	0.7	6.6	2.3	2.30E+05	2.27E+05	1.23	2.8E+05	8.5E+04	8.0E+05

* Char # = Characteristic Number: The number of positive tubes (out of 5 replicates) in decreasing order from the lowest dilution with 5 positive tubes.

MPN Data for Anaerobic Rate Study Microcosm Sample

Calculated at 4 Weeks, Test Tubes Incubated in Anaerobic Glove Box at 22 degrees C

Sample	Characteristic #	Dilution (first value)	MPN (from Table) min (95%C.I.)	max (95%CI)	Expected	Dilution correction MPN/g wet soil added	Wet/Dry soil ratio (estimated)
NRB >N_2 gas	5-1-0	0.00001	1.0	10.0	3.3	3.30E+05	1.21
FeRB	4-5-1	0.10	1.4	11.3	4.8	4.80E+01	1.21
SRB	1-0-0	0.10	0.0	1.0	0.2	2.00E+00	1.21
JP-4	5-1-0	0.001	1.0	10.0	3.3	3.30E+03	1.21
Total Het	5-3-0	0.00001	2.3	22.0	7.9	7.90E+05	1.21

MPN Soil Moisture Corrected MPN/g dry soil	95% Confindence Interval MPN min #/g dry wt	MPN max #/g dry wt
4.0E+05	8.3E+04	1.2E+06
5.8E+01	1.2E+01	1.4E+02
2.4E+00	1.7E-01	1.2E+01
4.0E+03	8.3E+02	1.2E+04
9.6E+05	1.9E+05	2.7E+06

APPENDIX H

MICROBIAL ACTIVITY

LABORATORY $^{14}CO_2$ MEASUREMENT RECORDS

C-14 Toluene dose 78899 DPM

Day 0: $^{14}CO_2$ Measurements

Day 0 of Toluene / CO2 flushing of COLD LAKE samples										
Sample Site	Flushed	Bottle 1 Fluor onl	Bottle 2 CO2	Bottle 3 CO2	um of total CO (= bottle 2+3)	Background	Sterile Control CO2	%14C converted	%14C added (averaged control)	%^{14}C recovered
Sterile Control FFTA 8 C/ 22 C	Oct-29	33751	963	54	1017	20	0	1.3	0	44.1
FFTA 22 C/8 C	Oct-29	39496	1201	85	1286	22	269	0.0		51.7
	Oct-29	43821	1354	112	1466	27	449	0.0		57.4
(dup)	Oct-29	44013	1380	92	1472	25	455	0.0		57.6
	Oct-29	32317	1115	89	1204	24	187	0.0		42.5
	Nov-02	29355	676	36	712	28	-305	0.0		38.1
	Nov-02	46579	841	68	909	28	-108	0.0		60.2
	mean	39264	1095	80	1175	26	158	0.0	0	51.3
Sterile Control FFTA Anaerobic	Nov-03	38633	786	39	825	16		1.0		50.0
FFTA Anaerobic	Nov-03	29500	460	37	497	16	-328	0.0		38.0
	Nov-03	29770	737	41	778	16	-47	0.0		38.7
	Nov-03	35012	668	52	720	16	-105	0.0		45.3
	mean	31427	622	43	665	16	-160	0.0		40.7
Sterile Control Old Imperial 8 C	Nov-03	19777	424	41	465	28		0.6		25.7
Old Imperial 8 C	Nov-02	20061	328	35	363	28	-102	0.0		25.9
	Nov-02	20990	198	36	234	28	-231	0.0		26.9
	Nov-02	25949	702	42	744	28	279	0.0		33.8
	mean	22333	409	38	447	28	-18	0.0		28.9

C-14 Toluene dose 78899 DPM

Day 3: $^{14}CO_2$ Measurements

Day 3 of Toluene / CO2 flushing of COLD LAKE samples										
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Background	Sterile Control CO2	%14C converted	%14C added (averaged control)	%^{14}C recovered
Sterile Control FFTA 8 C	Nov-03	44759	861	58	919	16		1.2		57.9
FFTA 8 C	Nov-03	36401	1492	98	1590	16	671	0.9		48.2
	mean				0					
Sterile Control FFTA 22 C	Nov-03	16403	645	48	693	16		0.9		21.7
FFTA 22 C	Nov-03	31688	1849	723	2572	16	1879	2.4		43.4
	mean				0					
Sterile Control FFTA 8 C Anaerobic					0					0.0
FFTA Anaerobic 8 C	Nov-03	18235	spilled	43		16				
	mean				0					
Sterile Control Old Imperial 8 C	Nov-03	31287	653	34	687	16		0.9		40.5
Old Imperial 8 C	Nov-03	42227	1185	58	1243	16	556	0.7		55.1
	mean									

C-14 Toluene dose 78899 DPM

Day 5: $^{14}CO_2$ Measurements

Day 5 of Toluene / CO2 flushing of COLD LAKE samples

Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Background	Sterile Control CO2	%14C converted	%14C added (averaged control)	% ^{14}C recovered
Sterile Control FFTA 8 C	Nov-05	28653	993	48	1041	23		1.3		37.6
FFTA 8 C	Nov-05	29996	2064	67	2131	23	1090	1.4		40.7
	Nov-05	47191	1500	71	1571	23	530	0.7		61.8
	Nov-05	20467	1467	45	1512	23	471	0.6		27.9
	mean	32551	1677	61	1738	23	697	0.9		43.5
Sterile Control FFTA 22 C	Nov-04	40785	908	148	1056			1.3		53.0
FFTA 22 C	Nov-04	23995	6507	276	6783		5727	7.3		39.0
	Nov-04	21615	5617	122	5739		4683	5.9		34.7
	Nov-04	8890	2179	82	2261		1205	1.5		14.1
	mean	22805	6062	199	6261		5205	6.6		36.8
Sterile Control FFTA 8 C Anaerobic	Nov-04	9397	113	43	156		0	0.2	0	12.1
FFTA Anaerobic 8 C	Nov-04	52652	1247	60	1307		1151	1.5		68.4
	Nov-04	44735	1138	59	1197		1041	1.3		58.2
	Nov-04	35197	1235	68	1303		1147	1.5		46.3
	mean	44195	1207	62	1269		1113	1.4		57.6
Sterile Control Old Imperial 8 C	Nov-05	31034	975	39	1014	23	0	1.3	0	40.6
Old Imperial 8 C	Nov-05	22594	2037	153	2190	23	1176	1.5		31.4
	Nov-05	27028	991	119	1110	23	96	0.1		35.7
	Nov-05	23564	1253	103	1356	23	342	0.4		31.6
	mean	24395	1427	125	1552	23	538	0.7		32.9

major leak, not included in calculations

C-14 Toluene dose 78899 DPM

Day 7: $^{14}CO_2$ Measurements

Day 7 of Toluene / CO2 flushing of COLD LAKE samples										
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Background	Sterile Control CO2	%14C converted	%14C converted (averaged control)	%^{14}C recovered
Sterile Control FFTA 8 C	Nov-06	10116	241	83	324	21	0	0.4	0	13.2
					900	avg value substituted for calculations due to apparatus failure.				
FFTA 8 C	Nov-06	28664	1610	66	1676	58	776	1.0		38.5
		16620	1340	46	1386	58	486	0.6		22.8
		31985	1556	42	1598	58	698	0.9		42.6
	mean	25756	1502	51	1553	58	653	0.8		34.6
Sterile Control FFTA 22 C	Nov-05	44444	649	83	732	23		0.9		57.3
FFTA 22 C	Nov-05	18366	2448	89	2537	23	1805	2.3		26.5
	broken vial									
	broken vial									
	mean	18366	2448	89	2537					26.5
Sterile Control FFTA 8 C Anaerobic	not tested									
FFTA Anaerobic 8 C	not tested									
Sterile Control Old Imperial 8 C	Nov-05	24346	634	53	687	23	0	0.9	0	31.7
Old Imperial 8 C	Nov-05	9164	784	58	842	23	155	0.2		12.7
	Nov-05	21834	1813	57	1870	23	1183	1.5		30.0
	Nov-05	23122	1292	44	1336	23	649	0.8		31.0
	mean	22478	1553	51	1603	23	916	1.2		30.5
	Leak in apparatus, not included in calculations									

C-14 Toluene dose 78899 DPM

Day 10: $^{14}CO_2$ Measurements

Day 10 of Toluene / CO2 flushing of COLD LAKE samples										
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Background	Sterile Control CO2	%14C converted	%14C converted (averaged control)	%^{14}C recovered
Sterile Control FFTA 8 C	Nov-06	25737	819	66	885	21	0	1.1	0	33.7
FFTA 8 C	Nov-06	26718	8105	264	8369	21	7484	9.5		44.5
	Nov-06	36042	3484	169	3653	21	2768	3.5		50.3
	Nov-06	21366	9470	410	9880	21	8995	11.4		39.6
(dup)	Nov-06			393						
	mean	28042	7020	309	7329		6444	8.2		44.8
FFTA 8 C +ve	Nov-09	broken								
8 C N+P	Nov-06	15311	19256	314	19570		18685	23.7		44.2
Sterile Control FFTA 22 C	broken				732	Day 7 value used for calculations				
FFTA 22 C	Nov-06	1913	30717	228	30945		30213	38.3		41.6
	Nov-06	1639	26218	559	26777		26045	33.0		36.0
dup	Nov-06	1685	26506	596	27102		26370	33.4		36.5
	Nov-06	2871	24686	929	25617		24885	31.5		36.1
dup	Nov-06	2896	24981	914	25895		25163	31.9		36.5
	mean	2201	26622	645	27267		26535	33.6		37.3
FFTA 22 C +ve	Nov-06	847	23369	696	24065		23333	29.6		31.6
+ve dup	Nov-06	835	23248	676	23924		23192	29.4		31.4
22 C N+P	Nov-06	772	24768	356	25124		24392	30.9		32.8
N+P dup	Nov-06	839	24967	355	25322		24590	31.2		33.2
Sterile Control FFTA 8 C Anaerobic	not sampled									
FFTA 8 C Anaerobic	not sampled									
Sterile Control Old Imperial 8 C	Nov-06	11647	1267	249	1516	24	0	1.9	0	16.7
Old Imperial 8 C	Nov-06	5999	2478	56	2534		1018	1.3		10.8
		23322	6396	263	6661		5145	6.5		38.0
		20828	6475	254	6729		5213	6.6		34.9
	mean	22075	6437	259	6695		5179	6.6		36.5
Old Imperial 8 C +ve	Nov-06	3382	17985	616	18601	24	17085	21.7	0	27.9
8 C N+P	Nov-06	11065	12546	317	12863	24	11347	14.4	0	30.3
	Leak in apparatus, excluded from calculations									

C-14 Toluene dose 78899 DPM

Day 14: $^{14}CO_2$ Measurements

Day 14 of Toluene / CO2 flushing of COLD LAKE samples									
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Sterile Control CO2	%14C converted	%14C converted (averaged control)	%^{14}C recovered
Sterile Control FFTA 8 C	Nov-08	30494	1117	378	1495	0	1.9	0	40.5
FFTA 8 C	Nov-06	8914	14544	632	15176	13681	17.3		30.5
		11252	13673	165	13838	12343	15.6		31.8
		10554	15444	281	15725	14230	18.0		33.3
	mean	10240	14554	359	14913	13418	17.0		31.9
FFTA 8 C +ve	Nov-11	565	16932	395	17327	15832	20.1		22.7
8 C N+P	Nov-11	750	27633	1005	28638	27143	34.4		37.2
Sterile Control FFTA 22 C	Nov-11	19208	206	91	297		0.4	0	24.7
FFTA 22 C	Nov-11	875	31670	405	32075	31778	40.3		41.8
		333	34130	1384	35514	35217	44.6		45.4
					0				
	mean	604	32900	895	33795	33498	42.5		43.6
FFTA 22 C +ve	Nov-11	377	32640	719	33359	33062	41.9		42.8
22 C N+P		533	33033	1331	34364	34067	43.2		44.2
Sterile Control FFTA 8 C Anaerobic	Nov-11	19499	423	78	501		0.6	0	25.3
FFTA Anaerobic 8 C	Nov-11	37036	821	68	889	388	0.5		48.1
		39027	1068	66	1134	633	0.8		50.9
		36866	1327	67	1394	893	1.1		48.5
	mean	37643	1072	67	1139	638	0.8		49.2
FFTA Anbc N+P	Nov-11	34016	929	61	990	489	0.6		44.4
Sterile Control Old Imperial 8 C	Nov-11	19099	542	48	590	0	0.7	0	25.0
Old Imperial 8 C	Nov-11	11370	18112	1086	19198	18608	23.6		38.7
		11482	13529	792	14321	13731	17.4		32.7
		13706	11387	782	12169	11579	14.7		32.8
	mean	12186	14343	887	15229	14639	18.6		34.7
	flour only = 26								

C-14 Toluene dose 78899 DPM

Day 24: $^{14}CO_2$ Measurements

Day 24 of Toluene / CO2 flushing of COLD LAKE samples									
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Sterile Control CO2	%14C converted	%14C converted (averaged control)	%^{14}C recovered
Sterile Control FFTA 8 C	Nov-09	20219	548	46	594	0	0.8	0	26.4
FFTA 8 C	Nov-09	499	29602	1103	30705	30111	38.2		39.5
	Nov-09	624	22861	558	23419	22825	28.9		30.5
		370	24240	1053	25293	24699	31.3		32.5
	mean	498	25568	905	26472	25878	32.8		34.2
FFTA 8C +ve	Nov-09	2794	26332	731	29063	28469	36.1		40.4
8 C N+P	Nov-09	340	30091	1425	31516	30922	39.2		40.4
Sterile Control FFTA 22 C	Nov-09	25629	404	79	483	0	0.6	0	33.1
FFTA 22 C	Nov-09	327	37551	1594	39145	38662	49.0		50.0
		416	38056	2255	40311	39828	50.5		51.6
		377	38368	2239	40607	40124	50.9		51.9
	mean	373	37992	2029	40021	39538	50.1		51.2
FFTA 22 C +ve	Nov-09	304	32153	1131	33284	32801	41.6		42.6
Sterile Control FFTA 8 C Anaerobic	Nov-09	36964	118	37	155	0	0.2	0	47.0
FFTA Anaerobic 8 C		34529	529	53	582	427	0.5		44.5
		33732	833	82	915	760	1.0		43.9
		51108	1466	66	1532	1377	1.7		66.7
	mean	39790	943	67	1010	855	1.1		51.7
FFTA Anbc N+P		42231	2084	85	2169	2014	2.6		56.3
Sterile Control Old Imperial 8 C	Nov-09	16913	457	35	492	0	0.6	0	22.1
Old Imperial 8 C	Nov-09	526	30731	1910	32641	32149	40.7		42.0
		15598	19836	1250	21086	20594	26.1		46.5
		1685	31446	1335	32781	32289	40.9		43.7
	mean	5936	27338	1498	28836	28344	35.9		44.1
Old Imperial 8 C +ve	Nov-09	487	33320	2748	36068	35576	45.1		46.3
8C N+P	Nov-09	1022	30090	1982	32072	31580	40.0		41.9

C-14 Toluene dose 78899 DPM

Day 32: $^{14}CO_2$ Measurements

Day 32 of Toluene / CO2 flushing of COLD LAKE samples									
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Sterile Control CO2	%14C converted	%14C converted (averaged control)	%^{14}C recovered
Sterile Control FFTA 8 C	Nov-10	22610	355	68	423	0	0.5	0	29.2
FFTA 8 C	Nov-10	1356	30079	864	30943	30520	38.7		40.9
		374	23294	1142	24436	24013	30.4		31.4
		342	30579	816	31395	30972	39.3		40.2
	mean	691	27984	941	28925	28502	36.1		37.5
FFTA 8C N+P		321	30594	1417	32011	31588	40.0		41.0
8 C +ve		319	34793	1171	35964	35541	45.0		46.0
Sterile Control FFTA 22 C		27839	326	77	403	0	0.5	0	35.8
FFTA 22 C		467	39190	1359	40549	40146	50.9		52.0
		408	40229	1019	41248	40845	51.8		52.8
		324	36201	698	36899	36496	46.3		47.2
	mean	400	38540	1025	39565	39162	49.6		50.7
FFTA 22C N+P		897	24637	788	25425	25022	31.7		33.4
22 C +ve		317	36827	882	37709	37306	47.3		48.2
Sterile Control FFTA 8 C Anaerobic	Nov-10	23827	397	71	468	0	0.6	0	30.8
FFTA Anaerobic 8 C	Nov-10	32815	1305	101	1406	938	1.2		43.4
		43016	1737	97	1834	1366	1.7		56.8
		42902	1868	81	1949	1481	1.9		56.8
	mean	39578	1637	93	1730	1262	1.6		52.4
FFTA Anbc N+P		38934	1629	86	1715	1247	1.6		51.5
Sterile Control Old Imperial 8 C	Nov-10	16958	509	55	564	0	0.7	0	22.2
Old Imperial 8 C		520	25136	1520	26656	26092	33.1		34.4
		4772	22636	1766	24402	23838	30.2		37.0
		420	23673	1559	25232	24668	31.3		32.5
	mean	1904	23815	1615	25430	24866	31.5		34.6
Old Imperial 8C N+P		314	21109	1383	22492	21928	27.8		28.9
+ve		375	28087	1071	29158	28594	36.2		37.4

C-14 Toluene dose 78899 DPM

Day 39: $^{14}CO_2$ Measurements

Day 39 of Toluene / CO2 flushing of COLD LAKE samples									
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Sterile Control CO2	%14C converted	%14C converted (averaged control)	% ^{14}C recovered
Sterile Control FFTA 8 C	Nov-17	47710	1019	59	1078	0	1.4	0	61.8
FFTA 8 C	Nov-17	596	29803	801	30604	29526	37.4		39.5
		308	30969	910	31879	30801	39.0		40.8
		705	31666	738	32604	31526	40.0		42.2
	mean	536	30879	816	31696	30618	38.8		40.9
FFTA 8C N+P	Nov-17	310	40444	1379	41823	40745	51.6		53.4
8 C +ve		255	33237	1356	34593	33515	42.5		44.2
Sterile Control FFTA 22 C	Nov-17	24370	372	82	454	0	0.6	0	31.5
FFTA 22 C	Nov-17	349	41301	2020	43321	42867	54.3		55.3
		259	32259	1631	33890	33436	42.4		43.3
		223	39468	965	40433	39979	50.7		51.5
	mean	277	37676	1539	39215	38761	49.1		50.1
FFTA 22C N+P	Nov-17	240	35772	1674	37446	36992	46.9		47.8
22 C +ve		192	40366	1690	42056	41602	52.7		53.5
Sterile Control FFTA 8 C Anaerobic	Nov-17	19879	483	49	532	0	0.7	0	25.9
FFTA Anaerobic 8 C	Nov-17	42228	1393	70	1463	931	1.2		55.4
		33910	2949	100	3049	2517	3.2		46.8
		44208	2766	123	2889	2357	3.0		59.7
	mean	40115	2369	98	2467	1935	2.5		54.0
FFTA Anbc N+P	Nov-17	35357	1888	98	1986	1454	1.8		47.3
Sterile Control Old Imperial 8 C	Nov-17	24875	574	47	621	0	0.8	0	32.3
Old Imperial 8 C	Nov-17	469	25056	2454	27510	26889	34.1		35.5
		287	25902	1645	27547	26926	34.1		35.3
		503	27411	779	28190	27569	34.9		36.4
	mean	420	26123	1626	27749	27128	34.4		35.7
Old Imperial 8C N+P	Nov-17	426	24194	583	24777	24156	30.6		31.9
+ve		3652	20307	1852	22159	21538	27.3		32.7

C-14 Toluene dose 78899 DPM

Day 46: $^{14}CO_2$ Measurements

Day 46 of Toluene / CO2 flushing of COLD LAKE samples									
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Sterile Control CO2	%14C converted	%14C converted (averaged control)	% ^{14}C recovered
Sterile Control FFTA 8 C	not sampled								
FFTA 8 C	not sampled								
FFTA 8C N+P 8 C +ve	not sampled								
Sterile Control FFTA 22 C	not sampled								
FFTA 22 C	not sampled								
	mean								
FFTA 22C N+P 22 C +ve									
Sterile Control FFTA 8 C Anaerobic	Nov-24	12484	366	78	444				16.4
FFTA Anaerobic 8 C	Nov-24	28422	4100	235	4335	3891	4.9		41.5
		33836	1534	133	1667	1223	1.6		45.0
	mean	31129	2817	184	3001	2557	3.2		43.3
FFTA Anbc N+P	not sampled								
Sterile Control Old Imperial 8 C	Nov-24	11313	203	42	245	0	0	0	14.6
Old Imperial 8 C	Nov-24	361	26160	2169	28329	28084	35.6		36.4
		4946	14112	1499	15611	15366	19.5		26.1
		2342	21618	2503	24121	23876	30.3		33.5
	mean	2550	20830	2057	22687	22442	28.4		32.0
Old Imperial 8C N+P +ve	not sampled								
Nov-24	flour only = 24 flour + carbasorb = 33								

C-14 Toluene dose 78699 DPM

Day 53: $^{14}CO_2$ Measurements

Day 53 of Toluene / CO2 flushing of COLD LAKE samples									
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Sterile Control CO2	%14C converted	%14C converted (averaged control)	% ^{14}C recovered
Sterile Control FFTA 8 C	not sampled								
FFTA 8 C	not sampled								
FFTA 8C N+P 8 C +ve	not sampled								
Sterile Control FFTA 22 C	Dec-01	24695	918	88	1006	0	0	0	32.6
FFTA 22 C	Dec-01	187	38219	4112	42331	41325	52.4		53.9
		266	47510	5093	52603	51597	65.4		67.0
		139	28457	2425	30882	29876	37.9		39.3
	mean	204	38062	3877	41939	40933	51.9		53.4
FFTA 22C N+P 22 C +ve	not sampled								
Sterile Control FFTA 8 C Anaerobic	Dec-01	12061	1041	905	1946	0	0	0	17.8
FFTA Anaerobic 8 C	Dec-01	30435	3916	529	4445	2499	3.2		44.2
		39749	5608	523	6131	4185	5.3		58.2
		45406	6704	520	7224	5278	6.7		66.7
	mean	38530	5409	524	5933	3987	5.1		56.4
FFTA Anbc N+P	not sampled								
Sterile Control Old Imperial 8 C	Dec-01	13856	2555	1337	3892				22.5
Old Imperial 8 C	Dec-01	368	28356	626	29162	25290	32.1		37.5
		208	24077	3009	27086	23194	29.4		34.6
		229	23792	5753	29545	25653	32.5		37.7
	mean	268	25408	3196	28604	24712	31.3		36.6
Old Imperial 8C N+P +ve	not sampled								
Dec-01	flour only = 25 flour + carbasorb = 41								
Bicarb Flow test	Apparatus 1		98.35 %		Apparatus 2	104.20 %			

C-14 Toluene dose 75899 DPM

Day 59: $^{14}CO_2$ Measurements

Day 59 of Toluene / CO2 flushing of COLD LAKE samples									
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Sterile Control CO2	%14C converted	%14C converted (averaged control)	% ^{14}C recovered
Sterile Control FFTA 8 C	Dec-07	39123	722	77	799	0	0	0	50.6
FFTA 8 C	Dec-07	217	34105	1262	35367	34568	43.8		45.1
		222	28572	691	29463	28664	36.3		37.6
		125	27517	1166	28683	27884	35.3		36.5
	mean	188	30065	1106	31171	30372	38.5		39.7
FFTA 8C N+P 8 C +ve		303	33725	1619	35344	34545	43.8		45.2
Sterile Control FFTA 22 C	not tested								
FFTA 22C	not tested mean								
FFTA 22C N+P 22 C +ve	not tested								
Sterile Control FFTA 8 C Anaerobic	Dec-07	19054	285	52	337	0	0	0	24.6
FFTA Anaerobic 8 C	Dec-07	30147	5419	295	5714	5377	6.8		45.5
		26251	3181	216	3397	3060	3.9		37.6
		33133	2574	201	2775	2438	3.1		45.5
	mean	29844	3725	237	3962	3625	4.6		42.8
FFTA Anbc N+P	not tested								
Sterile Control Old Imperial 8 C	Dec-07	17417	348	48	396	0	0	0	22.6
Old Imperial 8 C	Dec-07	189	31501	1470	32971	32575	41.3		42.0
		447	25659	1502	27161	26765	33.9		35.0
		162	27101	984	28085	27689	35.1		35.8
	mean	266	28087	1319	29406	29010	36.8		37.6
Old Imperial 8C N+P +ve	not tested								
	flour only = 26 flour + carbasorb = 57								

C-14 Toluene dose 78699 DPM

Day 73: $^{14}CO_2$ Measurements

Day 73 of Toluene / CO2 flushing of COLD LAKE samples									
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Sterile Control CO2	%14C converted	%14C converted (averaged control)	% ^{14}C recovered
Sterile Control FFTA 8 C	not tested								
FFTA 8C	not tested								
	mean								
FFTA 8C N+P 8 C +ve	not tested								
Sterile Control FFTA 22 C	21-Dec	23382	869	70	939	0	0	0	30.8
FFTA 22 C	21-Dec	601	46432	2116	48548	47609	60.3		62.3
		165	43394	3802	47196	46257	58.6		60.0
		249	50246	2846	53092	52153	66.1		67.6
	mean	338	46691	2921	49612	48673	61.7		63.3
FFTA 22C N+P 22 C +ve	21-Dec	780	27007	3324	30331	29392	37.3		39.4
		227	38837	1812	40649	39710	50.3		51.8
Sterile Control FFTA 8 C Anaerobic	21-Dec	25849	991	55	1046	0	0	0	34.1
FFTA Anaerobic 8 C	21-Dec	6371	28522	621	29143	28097	35.6		45.0
		37675	6546	550	7096	6050	7.7		56.7
		40783	6967	520	7487	6441	8.2		61.2
	mean	28276	14012	564	7292	6246	7.9		45.1
FFTA Anbc N+P	not tested								
Sterile Control Old Imperial 8 C	21-Dec	12567	645	77	722	0	0	0	16.8
Old Imperial 8 C	21-Dec	275	20526	4781	25307	24585	31.2		32.4
	21-Dec	188	26375	2058	28433	27711	35.1		36.3
	21-Dec	177	26666	3920	30586	29864	37.9		39.0
	mean	213	24522	3586	28109	27387	34.7		35.9
Old Imperial 8C N+P +ve	not tested								
	flour only = 27 flour + carbasorb = 59								

C-14 Toluene dose 78899 DPM

Day 88: $^{14}CO_2$ Measurements

Day 88 of Toluene / CO2 flushing of COLD LAKE samples									
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Sterile Control CO2	%14C converted	%14C converted (averaged control)	% ^{14}C recovered
Sterile Control FFTA 8 C	not tested								
FFTA	not tested								
	mean								
FFTA 8C 8C N+P 8 C +ve	not tested								
Sterile Control FFTA 22 C	not tested								
FFTA 22C	not tested								
	mean								
FFTA 22C N+P 22 C +ve	not tested								
Sterile Control FFTA 8 C Anaerobic	Jan-05	13181	275	106	381	0	0	0	17.2
FFTA	Jan-05	37371	2809	151	2960	2579	3.3		51.1
Anaerobic		41699	2994	247	3241	2860	3.6		57.0
8 C		28669	3000	182	3182	2801	3.6		40.4
	mean	35913	2934	193	3128	2747	3.5		49.5
FFTA Anbc N+P									
Sterile Control Old Imperial 8 C	not tested								
Old Imperial 8 C	not tested								
	mean								
Old Imperial 8C N+P +ve	not tested								
	flour only = 28 flour + carbasorb = 74								

C-14 Toluene dose 76899 DPM

Day 95: $^{14}CO_2$ Measurements

Day 95 of Toluene / CO2 flushing of COLD LAKE samples									
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Sterile Control CO2	%14C converted	%14C converted (averaged control)	% ^{14}C recovered
Sterile Control FFTA 8 C	Jan-12	43282	3095	415	3510	0	0	0	59.3
FFTA 8 C	Jan-12	516	34346	3342	37688	34178	43.3		48.4
	Jan-12	46789	3153	544	3727	217	0.3		64.0
		*Trial 2 excluded, vials likely mislabled							
	mean	516	34346	3342	37688	34178	43.3		48.4
FFTA 8C N+P 8 C +ve	not tested								
Sterile Control FFTA 22 C	not tested								
FFTA 22C	not tested mean								
FFTA 22C N+P 22 C +ve	not tested								
Sterile Control FFTA 6 C Anaerobic	Jan-12	12340	4778	1842	6620	0	0	0	24.0
					500	Use average value for calculations, contam. of sterile control likely			
FFTA Anaerobic 6 C	Jan-12	22063	1711	345	2056	1556	2.0		30.6
	Jan-12	45696	3221	439	3660	3160	4.0		62.6
	Jan-12	38837	4360	404	4764	4264	5.4		55.3
	mean	35533	3097	396	3493	2993	3.8		49.5
FFTA Anbc N+P									
Sterile Control Old Imperial 8 C	Jan-12	15650	990	148	1138	0	0	0	21.3
Old Imperial 8 C	Jan-12	711	27615	853	28468	27330	34.6		37.0
	Jan-12	354	29351	3738	33089	31951	40.5		42.4
	Jan-12	380	29403	6061	35464	34326	43.5		45.4
	mean	482	28790	3551	32340	31202	39.5		41.6
Old Imperial 8C N+P +ve	Jan-12	186	24764	5449	30213	29075	36.9		38.5
	flour only = 23			Bicarb Flow test					
	flour + carbasorb =	221		Apparatus 1	96.49	%	Apparatus 2	82.72	% (leaky test- rev flow)

C-14 Toluene dose 78699 DPM

Day 109: $^{14}CO_2$ Measurements

Day 109 of Toluene / CO2 flushing of COLD LAKE samples										
Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Background	Sterile Control CO2	%14C converted	%14C converted (averaged control)	% ^{14}C recovered
Sterile Control FFTA 8 C	not tested									
FFTA 8C	not tested									
	mean									
FFTA 8C N+P 8 C +ve	not tested									
Sterile Control FFTA 22 C	Jan-26	13178	335	81	416		0	0	0	17.2
FFTA 22 C	Jan-26	603	39275	550	39825		39409	49.9		51.2
		186	42693	1629	44322		43906	55.6		56.4
		406	38065	1119	39184		38768	49.1		50.3
	mean	428	40011	1099	41110		40694	51.6		52.6
FFTA 22C N+P 22 C +ve	Jan-26	2483	37098	2176	39274		38858	49.3		52.9
		1886	36104	847	36951		36535	46.3		49.2
Sterile Control FFTA 8 C Anaerobic	Jan-26	8611	129	71	200		0	0	0	11.2
FFTA Anaerobic 8 C	Jan-26	28574	2970	106	3076		2876	3.6		40.1
		37471	1692	133	1825		1625	2.1		49.8
		35944	2702	146	2848		2648	3.4		49.2
	mean	33996	2455	128	2583		2383	3.0		46.4
FFTA Anbc N+P	not tested									
Sterile Control Old Imperial 8 C	not tested									
Old Imperial 8 C	not tested									
	mean									
Old Imperial 8C N+P +ve	not tested									
	flour only = 28 flour + carbasorb = 147									

C-14 Toluene dose 78890 DPM

Day 123: $^{14}CO_2$ Measurements

Day 123 of Toluene / CO2 flushing of COLD LAKE samples

Sample Site	Flushed	Bottle 1 Fluor only	Bottle 2 CO2	Bottle 3 CO2	Sum of total CO2 (= bottle 2+3)	Sterile Control CO2	%14C converted	%14C converted (averaged control)	% ^{14}C recovered
Sterile Control FFTA 8 C	Feb-09	33469	338	35	373	0	0	0	42.9
FFTA 8 C	Feb-09	352	36203	207	36410	36037	45.7		46.6
	Feb-09	1053	27354	91	27445	27072	34.3		36.1
	mean	708	31779	149	31928	31555	40.0		41.4
FFTA 8C N+P	Feb-09	344	34556	893	35449	35076	44.5		45.4
8 C +ve		614	33212	267	33479	33106	42.0		43.5
Sterile Control FFTA 22 C	not tested								
FFTA 22C	not tested								
	mean								
FFTA 22C N+P 22 C +ve	not tested								
Sterile Control FFTA 6 C Anaerobic	Feb-09	8267	175	41	216	0	0	0	10.8
FFTA Anaerobic 8 C	Feb-09	34794	2880	94	2974	2758	3.5		47.9
	Feb-09	36594	3650	119	3769	3553	4.5		51.2
	Feb-09	3351	3714	85	3799	3583	4.5		9.1
	mean	24913	3415	99	3514	3298	4.2		36.0
FFTA Anbc N+P	Feb-09	33600	1648	87	1735	1519	1.9		44.8
Sterile Control Old Imperial 8 C	Feb-09	10639	1867	85	1952	0	0	0	16.0
Old Imperial 8 C	Feb-09	157	26277	2215	30492	28540	36.2		38.8
	Feb-09	331	37244	3418	40662	38710	49.1		52.0
	Feb-09	190	30856	2709	33565	31613	40.1		42.8
	mean	226	34050	3064	37114	35162	44.6		47.3
Old Imperial 8C N+P	Feb-09	163	22426	2232	24658	22706	28.8		31.5
+ve		293	55419	5586	61005	59053	74.8		77.7

dark adapted overnight in walk-in incubator — leak, omitted from calculations

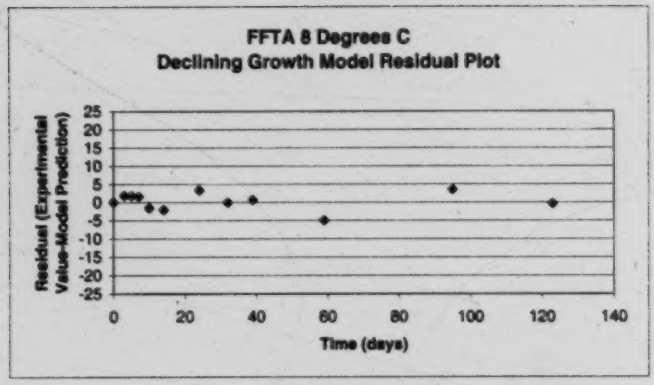
fluor only 28 DPM

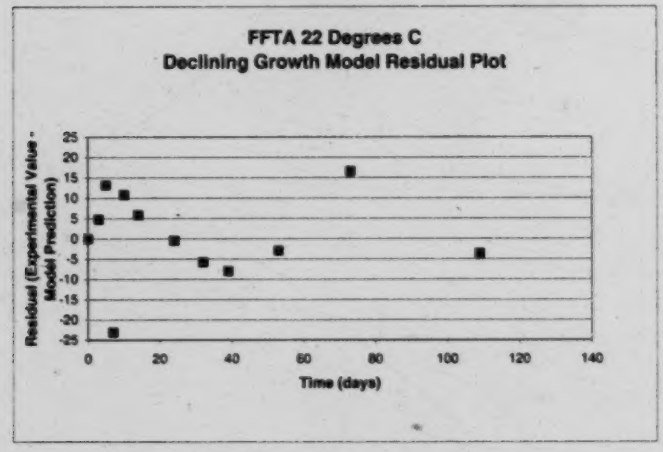
fluor plus Carbasorb 26 DPM (33 DPM less when dark adapted longer)

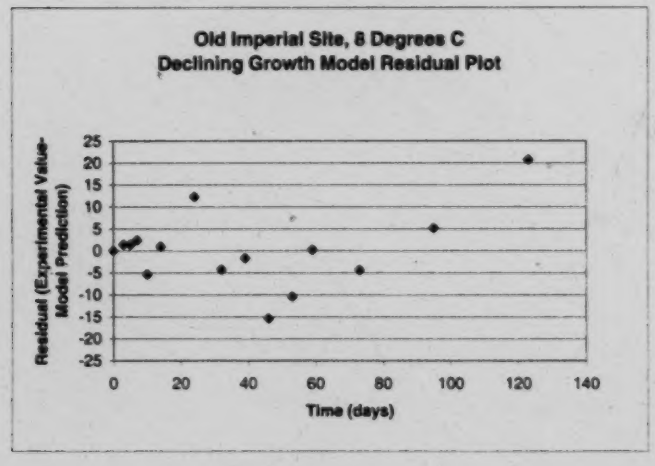
APPENDIX I

KINETIC MODELING OF MICROBIAL ACTIVITY

RESIDUAL PLOTS FOR THE DECLINING GROWTH MODEL


FFTA 8 Degrees C
Declining Growth Model Residual Plot
Residual (Experimental Value-Model Prediction)
25
20
15
10
5
0
-5
-10
-15
-20
-25
0
20
40
60
80
100
120
140
Time (days)


FFTA 22 Degrees C
Declining Growth Model Residual Plot
Residual (Experimental Value - Model Prediction)
25
20
15
10
5
0
-5
-10
-15
-20
-25
0
20
40
60
80
100
120
140
Time (days)


Old Imperial Site, 8 Degrees C
Declining Growth Model Residual Plot
Residual (Experimental Value-Model Prediction)
25
20
15
10
5
0
-5
-10
-15
-20
-25
0
20
40
60
80
100
120
140
Time (days)

APPENDIX J

CONTAMINANT FATE AND TRANSPORT MODELING

BIOPLUME II INPUT & OUTPUT DATA

BIOPLUME II
CONTAMINANT TRANSPORT UNDER THE INFLUENCE OF OXYGEN LIMITED BIODEGRADATION
INPUT DATA

GRID DESCRIPTORS

NX (NUMBER OF COLUMNS) = 11
NY (NUMBER OF ROWS) = 12
XDEL (X-DISTANCE IN FEET) = 100.0
YDEL (Y-DISTANCE IN FEET) = 100.0

TIME PARAMETERS

NTIM (MAX. NO. OF TIME STEPS) = 1
NPMP (NO. OF PUMPING PERIODS) = 1
PINT (PUMPING PERIOD IN YEARS) = 40.000
TIMX (TIME INCREMENT MULTIPLIER) = .00
TINIT (INITIAL TIME STEP IN SEC.) = 0.

HYDROLOGIC AND CHEMICAL PARAMETERS

S (STORAGE COEFFICIENT) = .000000
POROS (EFFECTIVE POROSITY) = .300
BETA (LONGITUDINAL DISPERSIVITY) = 10.0
DLTRAT (RATIO OF TRANSVERSE TO
LONGITUDINAL DISPERSIVITY) = .10
ANFCTR (RATIO OF T-YY TO T-XX) = 1.000000

EXECUTION PARAMETERS

NITP (NO. OF ITERATION PARAMETERS) = 7
TOL (CONVERGENCE CRITERIA - ADIP) = .0010
ITMAX (MAX.NO.OF ITERATIONS - ADIP) = 100
CELDIS (MAX.CELL DISTANCE PER MOVE
OF PARTICLES - M.O.C.) = .500
NPMAX (MAX. NO. OF PARTICLES) = 5000
NPTPND (NO. PARTICLES PER NODE) = 9

PROGRAM OPTIONS

NPNT (TIME STEP INTERVAL FOR COMPLETE PRINTOUT) = 1
NPNTMV (MOVE INTERVAL FOR CHEM. CONCENTRATION PRINTOUT) = 0
NPNTVL (PRINT OPTION-VELOCITY 0=NO; 1=FIRST TIME STEP; 2=ALL TIME STEPS) = 1
NPNTD (PRINT OPTION-DISP.COEF.0=NO; 1=FIRST TIME STEP; 2=ALL TIME STEPS) = 0
NUMOBS (NO. OF OBSERVATION WELLS FOR HYDROGRAPH PRINTOUT) = 1
NREC (NO. OF PUMPING WELLS) = 3
NCODES (FOR NODE IDENT.) = 1
NPNCHV (PUNCH VELOCITIES) = 0
NPDELC (PRINT OPT.-CONC. CHANGE) = 0

REACTION TERMS

DK (DISTRIBUTION COEFFICIENT) = .50000E-07
RHOB (BULK DENSITY OF SOLIDS) = .20000E+07
RF (RETARDATION FACTOR) = .13333E+01
THALF (HALF LIFE OF DECAY,IN SEC)= .00000E+00
DECAY (DECAY CONSTANT=LN 2/THALF)= .00000E+00

DECAY TERMS

DEC1 (ANAEROBIC DECAY COEFF.) = .13000E-01
DEC2 (REAERATION DECAY COEFF.) = .55000E-03

NODE IDENTIFICATION MAP

```
0 0 0 0 0 0 0 0 0 0 0
0 1 1 1 1 1 1 1 1 1 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 1 1 1 1 1 1 1 1 1 0
0 0 0 0 0 0 0 0 0 0 0
```

NO. OF NODE IDENT. CODES SPECIFIED = 1

THE FOLLOWING ASSIGNMENTS HAVE BEEN MADE:

CODE NO.	LEAKANCE	SOURCE CONC.	O2 CONC	RECHARGE
1	.100E+01	.00	4.50	

HEAD DISTRIBUTION - ROW
NUMBER OF TIME STEPS = 0
TIME(SECONDS) = .00000
TIME(DAYS) = .00000E+00
TIME(YEARS) = .00000E+00

	1	2	3	4	5	6	7	8	9	10	11
1	0	0	0	0	0	0	0	0	0	0	0
2	0	19.68	19.68	19.68	19.68	21.32	22.96	22.96	22.96	22.96	0
3	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0
7	0	0	0	0	0	0	0	0	0	0	0
8	0	0	0	0	0	0	0	0	0	0	0
9	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0
11	0	14.76	14.76	14.76	14.76	14.76	14.76	14.76	14.76	14.76	0
12	0	0	0	0	0	0	0	0	0	0	0

CONCENTRATION OF CONTAMINANT

0 mg/L

CONCENTRATION OF OXYGEN

4 mg/L

CUMULATIVE MASS BALANCE – (IN FT3)**

RECHARGE AND INJECTION = -.10098E+07
PUMPAGE AND E-T WITHDRAWAL = .00000E+00
CUMULATIVE NET PUMPAGE = -.10098E+07
WATER RELEASE FROM STORAGE = .00000E+00
LEAKAGE INTO AQUIFER = .59399E+08
LEAKAGE OUT OF AQUIFER = -.60331E+08
CUMULATIVE NET LEAKAGE = -.93140E+06
MASS BALANCE RESIDUAL = 78448.
ERROR (AS PERCENT) = .12995

RATE MASS BALANCE – (IN C.F.S.)

LEAKAGE INTO AQUIFER = .47056E-01
LEAKAGE OUT OF AQUIFER = -.47794E-01
NET LEAKAGE (QNET) = -.73786E-03
RECHARGE AND INJECTION = -.80000E-03
PUMPAGE AND E-T WITHDRAWAL = .00000E+00
NET WITHDRAWAL (TPUM) = -.80000E-03

1Y VELOCITIES AT NODES

0	0	0	0	0	0	0	0	0	0
0	6.7E-06	6.8E-06	6.4E-06	4.4E-06	7.3E-06	9.1E-06	7.0E-06	6.2E-06	0
0	6.4E-06	1.2E-05	1.9E-05	1.6E-05	1.5E-05	1.8E-05	5.9E-06	5.8E-06	0
0	6.3E-06	1.2E-05	1.9E-05	2.1E-05	1.6E-05	4.0E-06	7.8E-06	7.8E-06	0
0	1.8E-05	1.9E-05	2.2E-05	2.6E-05	3.4E-06	3.1E-06	3.4E-06	4.8E-06	0
0	1.4E-05	1.7E-05	2.3E-05	2.7E-05	2.5E-06	3.1E-06	3.7E-06	3.8E-06	0
0	2.9E-05	3.3E-05	4.0E-05	4.6E-05	7.7E-05	9.4E-05	1.1E-04	1.3E-04	0
0	1.5E-05	1.5E-05	1.6E-05	1.5E-05	9.8E-06	7.7E-06	6.8E-06	6.4E-06	0
0	1.5E-05	1.5E-05	1.4E-05	1.3E-05	1.1E-05	8.9E-06	7.9E-06	7.3E-06	0
0	1.4E-05	1.4E-05	1.4E-05	1.2E-05	1.1E-05	9.5E-06	8.4E-06	7.8E-06	0
0	7.1E-06	7.0E-06	6.7E-06	6.1E-06	5.4E-06	4.8E-06	4.3E-06	4.0E-06	0
0	0	0	0	0	0	0	0	0	0

STABILITY CRITERIA — M.O.C.

FLUID VELOCITIES
VMAX = 1.82E-05 VMAY = 1.27E-04
VMXBD= 1.82E-05 VMYBD= 2.63E-05
EFFECTIVE SOLUTE VELOCITIES
VMAX = 1.37E-05 VMAY = 9.49E-05
VMXBD= 1.37E-05 VMYBD= 1.97E-05
EFFECTIVE OXYGEN VELOCITIES
VMAX = 1.82E-05 VMAY = 1.27E-04
VMXBD= 1.82E-05 VMYBD= 2.63E-05

OUTPUT DATA

CONCENTRATION OF CONTAMINANT

```
NUMBER OF TIME STEPS =   1
     DELTA T      =  .12623E+10
     TIME(SECONDS) =  .12623E+10
  CHEM.TIME(SECONDS) =  .12623E+10
  CHEM.TIME(DAYS)   =  .14610E+05
     TIME(YEARS)  =  .40000E+02
  CHEM.TIME(YEARS)  =  .40000E+02
 NO. MOVES COMPLETED = 3195

0  0  0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  2  0  0  0  0  0
0  0  0  0  0  0 13  0  0  0  0  0
0  0  0  0  0  0  4  0  0  0  0  0
0  0  0  0  0  0  1  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0  0  0
```

CHEMICAL MASS BALANCE

```
    MASS IN BOUNDARIES    =  .00000E+00
    MASS OUT BOUNDARIES   = -.71486E+07
    MASS PUMPED IN        =  .20751E+09
    MASS PUMPED OUT       =  .00000E+00
    MASS LOST W. BIODEG.  =  .75804E+06
    MASS LOST BY RADIO. DCY=  .00000E+00
    MASS LOST BY ANAER. DCY= -.21587E+09
    MASS LOST BY REAER. DCY= -.92639E+07
    MASS ADSORBED ON SOLIDS=  .58279E+06
    INITIAL MASS ADSORBED =  .00000E+00
    INFLOW MINUS OUTFLOW  =  .20036E+09
    INITIAL MASS DISSOLVED =  .00000E+00
    PRESENT MASS DISSOLVED =  .99033E+06
    CHANGE MASS DISSOLVED =  .17484E+07
    CHANGE TOTL.MASS STORED=  .23312E+07
   COMPARE RESIDUAL WITH NET FLUX AND MASS ACCUMULATION:
    MASS BALANCE RESIDUAL =  -.27098E+08
    ERROR  (AS PERCENT)   =  -.13058E+02
```

CONCENTRATION OF OXYGEN

NUMBER OF TIME STEPS = 1
DELTA T = .12623E+10
TIME(SECONDS) = .12623E+10
CHEM.TIME(SECONDS) = .12623E+10
CHEM.TIME(DAYS) = .14610E+05
TIME(YEARS) = .40000E+02
CHEM.TIME(YEARS) = .40000E+02
NO. MOVES COMPLETED = 3195

0	0	0	0	0	0	0	0	0	0	0	0
0	0	4	4	5	4	4	4	4	4	4	0
0	0	4	5	5	4	4	4	4	4	4	0
0	0	4	5	5	3	0	4	4	4	4	0
0	0	4	5	4	0	0	4	4	4	4	0
0	0	4	4	4	0	0	4	4	4	4	0
0	0	4	4	4	2	0	3	4	4	4	0
0	0	4	4	4	3	0	3	4	4	4	0
0	0	4	4	4	4	2	3	4	4	4	0
0	0	4	4	4	4	3	4	4	4	4	0
0	0	4	4	4	5	5	4	4	4	4	0
0	0	0	0	0	0	0	0	0	0	0	0

CHEMICAL MASS BALANCE FOR OXYGEN

MASS IN BOUDARIES = .26732E+09
MASS OUT BOUNDARIES = -.28420E+09
MASS PUMPED IN = .00000E+00
MASS PUMPED OUT = .00000E+00
MASS LOST W. BIODEG. = .22741E+07
INFLOW MINUS OUTFLOW = -.16879E+08
INITIAL MASS DISSOLVED = .16200E+08
PRESENT MASS DISSOLVED = .15537E+08
CHANGE MASS DISSOLVED = .16115E+07
CHANGE TOTL.MASS STORED= .16115E+07
COMPARE RESIDUAL WITH NET FLUX AND MASS ACCUMULATION FOR OXYGEN:
MASS BALANCE RESIDUAL = -.18491E+08
ERROR (AS PERCENT) = -.69171E+01
COMPARE INITIAL MASS STORED WITH CHANGE IN MASS STORED FOR OXYGEN:
ERROR (AS PERCENT) = .55899E+02

STEADY-STATE FLOW

TIME INTERVAL (IN SEC) FOR SOLUTE-TRANSPORT SIMULATION = .12623E+10

LOCATION OF PUMPING WELLS

X	Y	RATE(IN CFS)	CONC.	CONC(02)
6	4	-.10E-03	424.00	.00
6	5	-.50E-03	220.00	.00
5	5	-.20E-03	60.00	.00

AREA OF ONE CELL = .1000E+05

X-Y SPACING:

100.00

100.00

TRANSMISSIVITY MAP (FT*FT/SEC)

	1	2	3	4	5	6	7	8	9	10	11
1	0	0	0	0	0	0	0	0	0	0	0
2	0	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0
3	0	0.0020	0.0040	0.0070	0.0070	0.0050	0.0050	0.0020	0.0020	0.0010	0
4	0	0.0020	0.0040	0.0070	0.0070	0.0050	0.0010	0.0020	0.0020	0.0010	0
5	0	0.0100	0.0100	0.0100	0.0100	0.0010	0.0007	0.0007	0.0010	0.0010	0
6	0	0.0200	0.0200	0.0200	0.0200	0.0010	0.0010	0.0010	0.0010	0.0010	0
7	0	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0
8	0	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0
9	0	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0
10	0	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0
11	0	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000	0
12	0	0	0	0	0	0	0	0	0	0	0

AQUIFER THICKNESS (FT)

.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	.0
.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	.0
.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	.0
.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	.0
.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	.0
.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	.0
.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	.0
.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	.0
.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	.0
.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	.0
.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0

DIFFUSE RECHARGE AND DISCHARGE (FT/SEC)

0.00E+00

NO. OF FINITE-DIFFERENCE CELLS IN AQUIFER = 90

AREA OF AQUIFER IN MODEL = .90000E+06 SQ. FT.

NZCRIT (MAX. NO. OF CELLS THAT CAN BE VOID OF PARTICLES; IF EXCEEDED, PARTICLES ARE REGENERATED) = 2